ORGANOMETALLIC COMPLEXES

OF NICKEL,

PALLADIUM AND PLATINUM

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T H E S I S

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A B S T R A C T.

We have examined the action of organomercury reagents on complexes of the nickel group in an attempt to find a cleaner route to the organotransition-metal compounds, and in the hope of clarifying the mechanisms involved in these reactions.

The reactions between R_2Hg (R = Ph or Me) and $(R_3P)_2MCl_2$ (M = Ni, Pd or Pt) yield RHgCl and trans-$(R_3^1P)_2$ MRCl. The reactions with R = Ph proceed more readily than those with R = Me. Reverse reactions between $HgCl_2$ and $(R_3^1P)_2$ MR_2 produce the same products.

R_2Hg and the carbonyl complexes $(R_3^1P)(CO)PtCl_2$ react to give RHgCl and the previously unknown chlorine-bridged compounds $(R_3^1P)_2Pt_2(COR)_2Cl_2$. No carbonyl insertion is observed when RLi replaces R_2Hg, and Grignard reagents lead to a complex mixture of products. Possible mechanisms of the mercurial reactions are discussed.

It seems that the synthetic value of the reactions is small, except for those involving carbonyl insertion. The halogen-bridged binuclear acyl complexes are produced in good yield and can be converted into other derivatives by bridge-splitting reactions using tertiary phosphines or cyclopentadienyl thallium, for example.

Till now, very few cyclopentadienyl complexes of palladium or platinum have been reported. We investigated the possibility of using dicyclopentadienyl mercury as an agent to introduce the C_5H_5 ligand to complexes of the nickel group. Although we have spectroscopic evidence that $(C_5H_5)_2Hg$ can be so utilised, no organometallic complexes could be isolated from the reaction mixtures due to decomposition of the organomercury by-products.

We find, however, that the binuclear halogen-bridged complexes $(R_3P)_2Pd_2X_4$ (R = Et, ^iPr or Ph; X = Cl, Br or I) react with cyclopentadienyl thallium to produce $(\pi\text{-}C_5H_5)(R_3P)PdX$. Yields are poor when analogous platinum complexes are used, but halogen-bridged organoplatinum compounds $(R_3P)_2Pt_2R^1{}_2X_2$ give good yields of $(\pi\text{-}C_5H_5)(R_3P)PtR^1$ (R = Et; R^1 = Ph or o-tolyl: R = Bu^n; R^1 = COPh).

The complexes $(\pi\text{-}C_5H_5)(R_3P)MX$ (M = Pd or Pt) react with tertiary phosphines to give either ionic π-bonded derivatives $[(\pi\text{-}C_5H_5)(R_3P)_2M]^+X^-$ or unstable σ-bonded compounds $(R_3P)_2M(\sigma\text{-}C_5H_5)X$, depending on the nature of the solvent and the tertiary phosphine. The same complexes can be produced from $(R_3P)_2MX_2$ and C_5H_5Tl.

The nickel complexes $(R_3P)_2NiX_2$, on the other hand, react with C_5H_5Tl or $(C_5H_5)_2Hg$ to yield $(\pi\text{-}C_5H_5)(R_3P)NiX$.

The diarsine complex $[C_6H_4(AsEt_2)_2]\ Pt(\sigma\text{-}C_5H_5)Cl$, produced from $[C_6H_4(AsEt_2)_2]\ PtCl_2$ and C_5H_5Tl, is stable in air to 130°. Less stable σ-bonded cyclopentadienyl complexes can be prepared from the reactions of $(\pi\text{-}C_5H_5)(R_3P)PtR^1$ with R_3P or CO, or cis-$(R_3P)(CO)PtCl_2$ with C_5H_5Tl.

The palladium complex $(\pi\text{-}C_5H_5)(Et_3P)PdBr$ reacts with C_5H_5Tl to produce the novel derivative $(\pi\text{-}C_5H_5)(\sigma\text{-}C_5H_5)Pd(PEt_3)$. Reaction between hydrazine hydrate and $(\pi\text{-}C_5H_5)(R_3P)PdBr$ (R = Et or ^iPr) gives the phosphido-bridged complexes $[(\pi\text{-}C_5H_5)PdPR_2]_2$. The physical techniques of ^1H n.m.r., i.r. and mass spectroscopy were applied in the characterisation of all the complexes.

The platinum derivative $C_{20}H_{20}Pt_2$, first reported by German workers in 1967, has been re-investigated by X-ray analysis. The complex contains a platinum-platinum bond, with a π-cyclopentadienyl ring bound to each metal atom. The most interesting feature of the structure is the presence of the hitherto unsuspected 5-(5^1-cyclopentadienyl)-cyclopentadiene unit bridging the two metal atoms.

Finally, we note that facile $\pi \longrightarrow \sigma$ rearrangement of C_5H_5 rings is a dominant feature in the chemistry of the cyclopentadienyl complexes of nickel, palladium and platinum, and this interconversion is discussed at several points in the text.

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SECTION 2. CYCLOPENTADIENYLS OF PALLADIUM AND PLATINUM.

INTRODUCTION

Historical Background

One of the most important developments in chemistry in the last twenty years has been the synthesis and study of many organometallic derivatives of the transition metals. It was in 1831 that Zeise, a Danish pharmacist, reported the first organometallic complex,[1] an ethylene derivative of platinum, which has since been shown to have the composition $[(C_2H_4)Cl_3Pt]^-K^+$. From then till the early 1950's, however, work on transition metal organic derivatives was rather limited. Thus, by 1950, the organic chemistry of the transition elements comprised little more than the methyl platinum IV compounds of Pope and Peachy[2], the organo-gold complexes prepared by Gibson[3], the olefin complexes of platinum and palladium which were not understood, and Hein's phenyl-chromium compounds (1919-1931), the nature of which was also unknown.

The impetus to fresh work was given in 1951 with the discovery[4] of ferrocene, $Fe(C_5H_5)_2$, and with the recognition of its sandwich-like structure. It soon became clearly recognised that the ability to form metal-carbon bonds was a general property of all the d-group transition metals.

Description of metal-carbon bond types

The simplest type of metal-carbon bond is a localised 2-electron covalent bond, and the ligands forming bonds of this nature with the metal are formally 1-electron donors. They are generally alkyl or aryl groups, although alkyl, cyclopentadienyl or alkynyl ligands also form a limited number of such complexes. By far the most widely applied method for the formation of these metal-carbon σ-bonds is the reaction of a metal halide or related compound with an anionic alkylating or arylating agent.

$$L_n M - X + R - M^1 \longrightarrow L_n M - R + M^1 X$$

Agents that have been used include organo compounds of alkali metals, magnesium and zinc.

$$cis\text{-}(Et_3P)_2 PtCl_2 + \text{excess } PhLi \longrightarrow cis\text{-}(Et_3P)_2PtPh_2 + 2LiCl \quad (5)$$

$$(\pi\text{-}C_5H_5)_2 TiCl_2 + MeMgCl \longrightarrow (\pi\text{-}C_5H_5)_2 TiMeCl + MgCl_2 \quad (6)$$

$$2NbCl_5 + 3ZnMe_2 \longrightarrow 2Me_3 NbCl_2 + 3ZnCl_2 \quad (7)$$

The stability of the alkyl or aryl derivatives depends on the nature of the metal and the other ligands (if any), as will be shown later.

A typical 2-electron donor hydrocarbon ligand is ethylene. Ethylene, like carbon monoxide and tertiary phosphines, belongs to that class of ligand which does not often co-ordinate readily with traditional acceptor molecules like the Lewis acid BF_3, for example, but which

forms quite stable complexes with transition metals which have available d-electrons. It is generally believed[8] for ligands of this type that bonding with the metal involves both a simple σ-co-ordinate link due to donation of 2 electrons from the ligand to empty d orbitals in the metal, and also involves a back-donation of the metal electrons in d orbitals to empty ligand anti-bonding orbitals of appropriate symmetry. The type of bond utilised in the latter case is a π-bond. The conventional pictorial representations of the bonding of ethylene to a metal are shown in figure 1. They are alternatives in the light of a molecular orbital approach but can be used to emphasise the relative importance of the contribution to the ligand-metal bond of σ-bonding (a) or π-bonding (b).

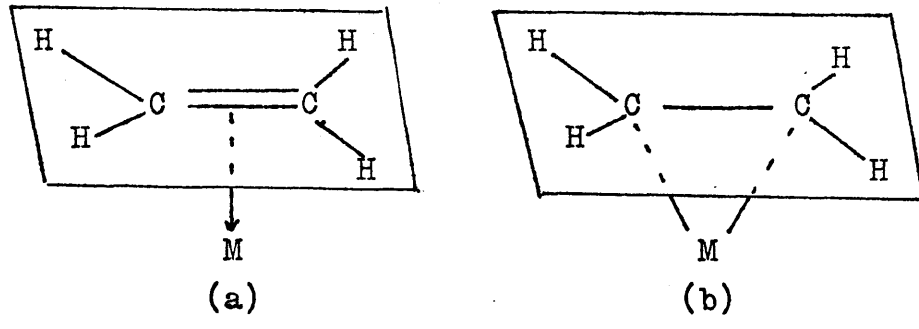
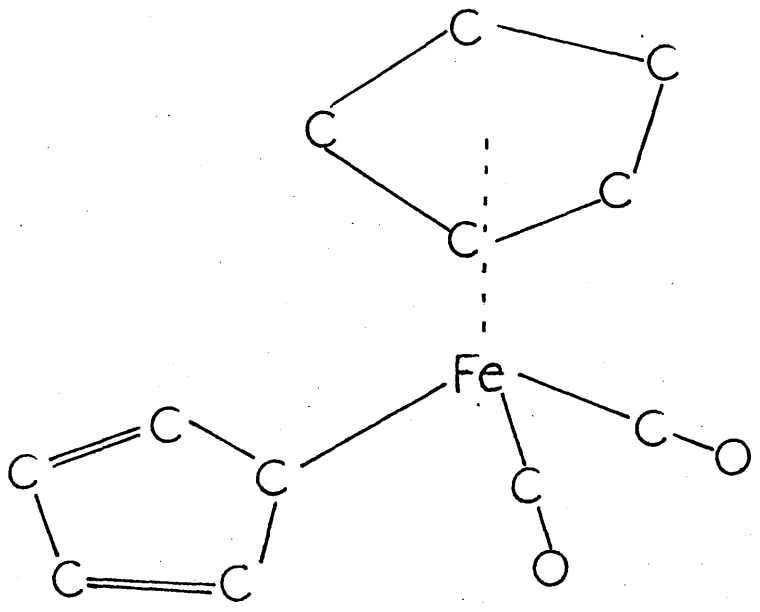


Figure 1. Representations of the olefin metal bond.

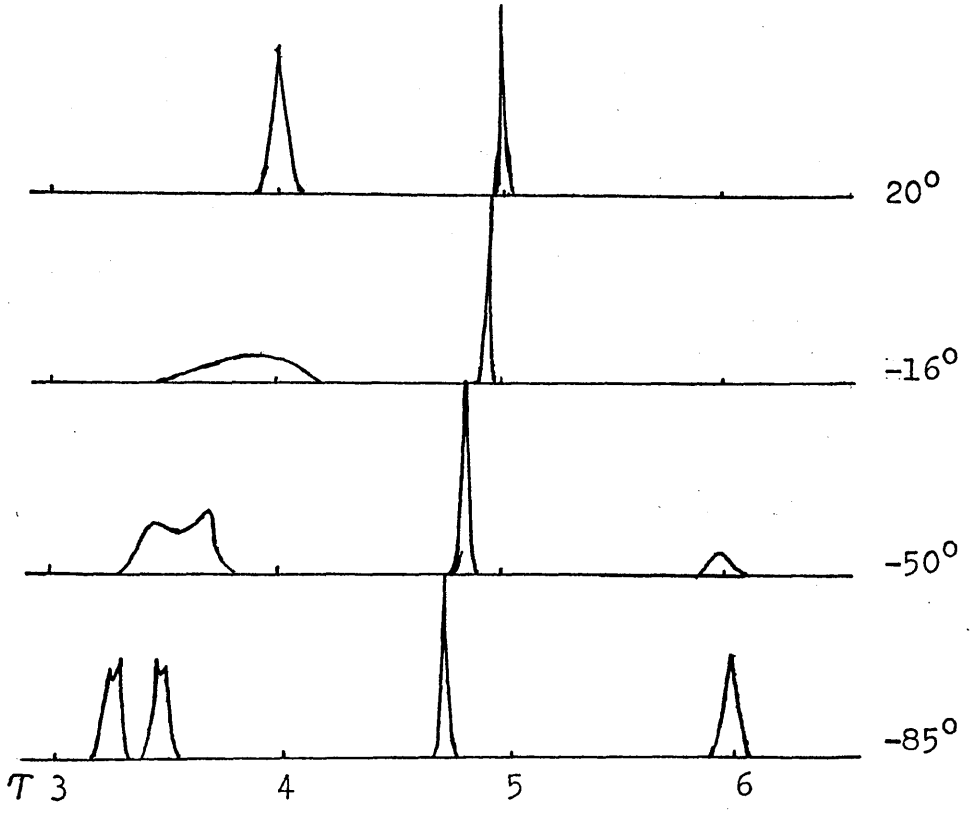
π-Bonding is involved to some extent when a metal interacts with any hydrocarbon ligand which formally donates more than 1 electron. The metal is normally equidistant from the carbon atoms involved in the bonding and the π-electrons are delocalised over these carbon atoms.

An interesting example of a complex which contains both π- and σ-bonded organic ligands is $(C_5H_5)_2$ Fe $(CO)_2$. An x-ray investigation[8] of this material yields the structure shown in figure 2(a). One of the cyclopentadienyl rings is bound to the iron atom by means of a 2-electron covalent bond, the Fe-C bond length being 2.11Å. The carbon-carbon distances within this ring show some differences from the pattern expected for a cyclopenta-2,4-diene ring but the standard deviations are such that no significance can be attached to this. All the carbon atoms of the other ring are equivalent, demonstrating that the ring is symmetrically π-bonded. The mean Fe-C distance is 2.08Å.

This complex also exhibits an interesting fluxional behaviour. It has been studied[8] by variable temperature n.m.r. spectroscopy, and spectra observed at various temperatures are shown in figure 2(b). The room temperature spectrum shows two single resonances, one



(a) Structure of $(C_5H_5)_2Fe(CO)_2$



(b) N.m.r. spectra at various temperatures

FIGURE 2.

for the protons of the π-cyclopentadienyl ring and one for the protons of the σ-bonded group. As the solution is cooled the peak associated with the σ-cyclopentadienyl protons broadens and collapses and by -85° peaks consistent with the AA' BB' X system expected for the σ-C_5H_5 group have appeared. On the basis of this evidence it has been proposed that at room temperature the σ-C_5H_5 ring is rapidly changing the carbon atom which bonds to the metal by a rotational intra-molecular mechanism involving 1,2 shifts. The shape of the peak associated with the π-cyclopentadienyl protons remains invariant with temperature showing that all the protons of this ring remain equivalent.

X-ray structural determinations have been performed on a wide range of π-complexes such as $(\pi\text{-}C_3H_5)PdCl_2$,[9] $(\pi\text{-}C_4Ph_4)Fe(CO)_3$,[10] $(\pi\text{-}C_6H_6)_2Cr$[11], $(\pi\text{-}C_7H_7)V(\pi\text{-}C_5H_5)$[12] and $(C_8H_8)Mo(CO)_3$.[13] In addition to x-ray crystallography other physical techniques such as infra-red, ultraviolet, nuclear magnetic resonance and mass spectroscopy have enabled many novel complexes to be characterised.

One of the by-products of the intense investigation of organometallic chemistry has been the discovery that transition metal complexes can be utilised as catalysts

in industrial processes such as carbonylation, polymerisation, isomerisation or hydrogenation of olefins. Olefin polymerisation by transition metal compounds, such as those used in the catalyst systems of Ziegler and Natta, can be remarkably stereospecific and can lead to polymers with improved properties to those prepared by conventional high-pressure, free radical polymerisation. In many of these catalytic processes a necessary step is the conversion of a π-bonded organic system to a σ-bonded one.

Parallel to the development of the preparative and catalytic aspects of organometallic chemistry, the nature of the bonding in the complexes has also been investigated. In a general sense a stable compound is resistant to degradation by heat, oxidation or hydrolysis. By any criterion, transition metal alkyls, which have only alkyl ligands on the metal atom, are often very unstable. Dimethylmanganese, for example, is a spontaneously flammable solid which explodes on impact. Most other simple transition metal alkyls also seem to be thermodynamically unstable relative to hydrocarbon decomposition products and the free metal. In contrast to this, some metal complexes bearing other ligands in addition to alkyl or aryl groups are strikingly stable. Thus, the bond energy of the Pt-C bond in

trans - $(Et_3\ P)_2\ Pt\ Ph_2$ is about 60 K.cal./mole[14], roughly equal to that of a C-C bond in an alkane.

In many metal- σ -organo complexes it seems probable that the first step in their decomposition is the dissociation of the metal-carbon bond. This may dissociate homolytically or heterolytically, forming either a carbon radical or carbon ion species. In both cases, the carbon fragments would be very reactive and readily form stable products, by polymerisation for example.

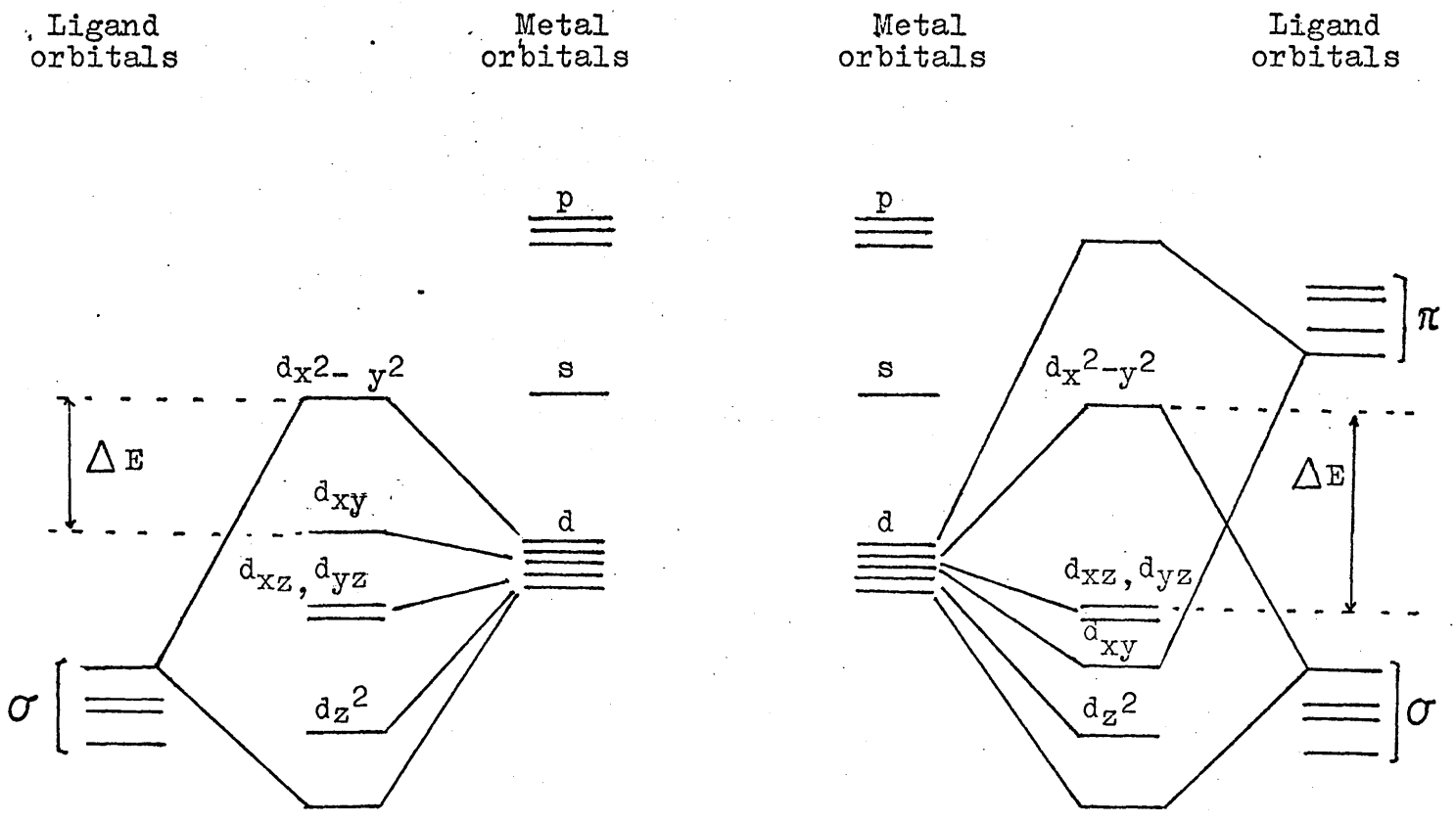
Stability Theories.

Chatt and Shaw have given a detailed argument[15] for the kinetic stability of the complexes $L_2\ MR_2$ and $L_2\ MRX$ [L = a π-bonding ligand such as a tertiary phosphine, R = alkyl, aryl or ethynyl, X = halogen and M = Ni, Pd or Pt] in which they assume that the rate-determining step in the decomposition of these complexes is the homolytic fission of the M-R bond.

Homolytic dissociation is imagined to proceed either by the promotion of an electron into the anti-bonding orbital of the M-C bond, or the promotion of one electron from the M-C bonding orbital. It follows that the energy barrier to homolytic dissociation can be equated with the energy difference ($\triangle$ E) between, either the

M-C anti-bonding orbital and the highest filled orbital, or the M-C bonding orbital and the lowest unfilled orbital, whichever process operates. The larger the value of ΔE, the greater the kinetic stability of the metal-carbon bond to dissociation.

A schematic energy level diagram for square-planar complexes, showing the energy gap ΔE between the highest filled and the lowest unfilled molecular orbitals, is given in figure 3. Figure 3(a) represents the case when there is only σ-bonding and 3(b) shows how ΔE is increased when there is a π-bonding interaction in the dxy plane. Several factors, which may cause an increase in ΔE and hence an increase in the thermal stability of the complexes, have been discussed. Firstly, the effect of increasing atomic number in the series Ni, Pd, Pt, is that the interaction of the metal d x^2-y^2 and the ligand orbitals increases, raising ΔE. This argument partly accounts for the observed increase in thermal stability of the organic derivatives in the order Pt > Pd > Ni. Secondly, the presence of π-bonding ligands in these complexes causes the utilisation of the metal dxy, dxz and dyz orbitals. Bonding interactions of these orbitals with the ligands forms M.O.s of lower energy than that of the previously non-bonding d orbitals, increasing ΔE.



Schematic energy level diagrams for square-planar complexes.

FIGURE 3.

In agreement with this, the order of thermal stability of L_2 Ni R_2, where R = alkynyl > aryl > alkyl is found, which is the order of decreasing π-bonding ability of the organic ligand. It is also significant that the most stable transition metal alkyls are those of the heavier group VIII metals that contain tertiary phosphine ligands. In the theory of Chatt and Shaw, it is the ability of phosphorus to participate in π-bonding with the metal which increases ΔE and confers great stability on these complexes.

However, Pidcock and co-workers in a study of Pt^{195} - P^{31} nuclear spin coupling constants concluded[16] that phosphorus exerts a high trans influence by means of a σ-bonding mechanism. They examined the P^{31} n.m.r. spectra of complexes of the type cis- and trans-$(Bu_3P)_2$ Pt X_2 and cis- and trans-$(Bu_3P)_2$ Pt_2X_4. Neglecting any π-interactions they discussed J(Pt-P) in terms of the s-component of the platinum-phosphorus bond and were able to rationalise their results on this basis.

Parshall has studied[17] the F^{19} shielding parameters of some meta- and para-fluorophenyl platinum complexes and has shown that the parameters are greatly affected by the electronic nature of the ligand trans to the aromatic group.

For derivatives containing the triethylphosphine ligand trans to the aryl group, he deduced that Et_3P is a σ-donor of comparable strength to an aryl group but no meaningful estimate of the π-acceptor character of Et_3P could be obtained. Recently,[18] the method has been applied to the complexes (R_3P) Au C_6H_4F-m and -p. These compounds provide an ideal system for such a study since the molecules are linear and no other interfering groups are present. The π-acceptor ability of the ligands was found to be Bu_3 P~Et_3 P~Me_2 PhP < (p-Me $C_6H_4)_3$ P~Ph_3P < (C_6F_5) Ph_2P < $(PhO)_3P$. This is in agreement with generally held ideas that electron withdrawing substituents on phosphorus increase the π-acceptor strength.

Thus, in some cases, it would appear that π-bonding might make a significant contribution to bonds between metal ions and heavy donor atoms. π-bonding will become more important when ligands with strong electronegative substituents, such as PF_3, are used in conjunction with Lewis acids of very low formal oxidation state, as in $(F_3P)_4$ Pt.

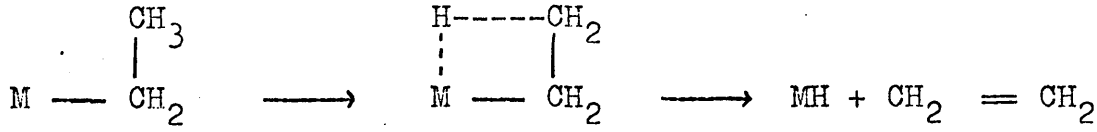
Nevertheless, whether phosphines are bound by π-bonds, σ-bonds or a combination of both, their net effect appears to be to stabilise the σ-bonded organometallic complexes.

The theory of Chatt and Shaw can explain the stability of most square-planar σ-organometallic complexes simply by consideration of the magnitude of ΔE. There are, however, several types of complex whose stability cannot be accounted for solely in this manner. For example, nickel aryl complexes trans-$(R_3P)_2$ Ni Ar_2 are markedly more stable when the aromatic ring is ortho-substituted than when it is meta-, para- or un-substituted.[19] In the case of ortho-substituted aryls, models show that the ortho-substituents would be held above and below the xy-plane of the metal. In this configuration the aryl π^*-orbitals can interact only with the dxy orbital and the increase in ΔE would thus be greater than if interaction with dxz and dyz orbitals also occurred. The ortho-substituents also interact so as to stabilise the square-planar configuration about the metal and prevent rearrangement to a tetrahedral complex. They may also sterically inhibit the attack of ligands along the z-axis.

Square-planar organo nickel complexes containing secondary alkyl phosphines, such as Pr_3^iP are also remarkable in their stability compared to the primary alkyl phosphine derivatives. Thus, the compounds trans-$(Pr_3^iP)_2$ Ni RCl[R = H, Me]are quite stable[20]

whereas their Pr_3^nP analogues are unknown. Since it cannot be argued that differences in phosphorus-nickel bonding account for the marked increase in stability, Green[20] has suggested that a steric factor must be important. The mechanism of stabilisation may be related to the observation that in the 2^y alkylphosphine complexes the bulkiness of the 2^y alkyl group restricts the deformation of the trans square-planar nickel co-ordination to a tetrahedral form.

It has been observed experimentally that for a number of metal-alkyl complexes the thermal stability decreases in the order Me > Et > Pr. The decrease in stability with increasing length of the alkyl chain may be explained by interaction of the metal atom with a β-substituent.



A transition state of lower energy than required for unaided dissociation would be formed in this case.

We have discussed some of the factors influencing the stability of the bis-phosphine organo complexes of

the nickel group, and now some of their properties will be described.

Organic complexes of the nickel group

Although it was not until 1957 that the compounds were first reported,[21] by 1960 a considerable number of complexes of the form $(R_3P)_2MR^1_2$ and $(R_3P)_2MR^1X$[M = Ni[19], Pd[22], Pt[5,23]; R^1 = alkyl, aryl] were known, the complexes being prepared by the standard technique of treating the bis-phosphine metal dihalide with Grignard or organolithium reagents. As the stability of these derivatives decreases in the order Pt > Pd > Ni, organo-nickel II compounds have proved very difficult to prepare in the pure state, and in the original work[19] by Chatt and Shaw only when R^1 was an ortho-substituted aryl group, or an ethynyl or substituted ethynyl group could a series of stable organo-nickel complexes of the types $(R_3P)_2NiR^1X$ and $(R_3P)_2NiR^1_2$ be isolated. Recently, however, it has been reported that if bulky phosphines such as triisopropylphosphine or tricyclohexylphosphine are co-ordinated to nickel, derivatives such as trans-$(Pr^i_3P)_2NiMeX$ [X = Cl,Br,I][20] or trans-$(cy_3P)_2NiHMe$[24] can be isolated (vide infra).

In the case of palladium, the square planar complexes $(R_3P)_2PdR^1X$ and $(R_3P)_2PdR^1_2$ [R^1 = alkyl, aryl]

are well characterised.[22] Although they are more stable than the nickel analogues, many are unstable and decompose slowly at room temperature. As found for the nickel complexes, palladium aryls have the trans-configuration. The alkyl compounds are also normally isolated as the trans-isomers, although a few relatively unstable cis-isomers are known. Apart from phosphine ligands, stable alkyl palladium derivatives have been prepared in which the π-bonding ligand is a chelate olefin, 2,2[1]-bipyridyl or 1,2-dithiomethylethane.

σ-Bonded organic complexes of platinum are amongst the most stable organo transition metal compounds known.[25] The great variety of known organoplatinum II compounds makes a comparison of their equally diverse properties difficult. Most of the compounds isolated are colourless or pale yellow crystalline solids, stable to air and water and soluble in organic solvents. The lower members of the more stable series can be distilled without decomposition. As for the palladium complexes, Chatt and Shaw[5,23] observed that the stability of the alkyl platinum derivatives decreased in the order

Me > Et > n-Pr > n-Bu > benzyl.

Platinum is unique in the group in that organo derivatives of the type $R^1 (R_3P) Pt (\mu - X)_2 Pt (R_3P) R^1$ [X = Br, I,] can be prepared from the reaction between

Grignard or organolithium reagents and the corresponding binuclear halogen bridged complex. Compounds with $R_2 P, R_2 As$ and RS bridging groups have also been prepared in this way.[26] It was found,[22] however, that a single strong donor co-ordinated to palladium was inadequate to stabilise a binuclear methyl palladium derivative with halogen bridges.

An interesting reaction of alkyl and aryl derivatives of the late transition elements is insertion of carbon monoxide into the metal-carbon bond with formation of acyl complexes. This type of reaction has been reported for Mo, Mn, Fe, Co, Ni, Pd and Pt compounds, and insertion of CO into the cobalt-carbon bond of cobalt carbonyl derivatives is a key step in the 'OXO' reaction and catalytic carboxylation processes.

Booth and Chatt found[27] that the monomethyl complex of palladium, trans-$(Et_3 P)_2$ Pd Me X [X= Cl, Br,] carbonylated at atmospheric pressure and temperature to form trans-$(Et_3 P)_2$ Pd (CO Me) X, whereas the analogous platinum compound required heating at 90° under a pressure of CO to form trans-$(Et_3 P)_2$ Pt (CO Me) X. These observations may reflect the much greater stability of the Pt-C bond in the starting material compared with the Pd-C bond. Higher temperatures, ca. 120°, were required

to produce the benzoyl derivatives $(Et_3\ P)_2\ Pt\ (CO\ Ph)X$.

The initial step in these reactions is thought to be co-ordination of the CO molecule to the metal atom to give 5- or 6- co-ordinate intermediates. This is supported by the work of Wright, who showed[28] that carbon monoxide can transfer from the co-ordination sphere of platinum and insert into a platinum-carbon bond.

$$(C_8H_{17})\ Pt\ (CO)Cl_2 + 4Ph_3P \longrightarrow 2(Ph_3P)_2Pt(CO\ C_8H_{17})Cl$$

A property of the acyl complexes is that when they are heated above their melting point, decomposition with initial evolution of carbon monoxide and formation of the corresponding alkyl or aryl derivatives occurs. The derivative can be isolated when it is sufficiently stable thermally, for example trans-$(Et_3\ P)_2\ Pt\ (CO\ Me)\ I$ on heating yields trans-$(Et_3P)_2\ Pt\ Me\ I$.[27] This decarbonylation, which is the reverse of the reaction of formation, is typical of most acyl compounds of transition metals. The general properties of the acyl complexes are very similar to those of the corresponding alkyl or aryl derivatives. Thus, trans-$(Et_3\ P)_2\ Ni\ (CO\ Me)\ Cl$ is unknown and trans-$(Et_3\ P)_2\ Pd\ (CO\ Me)\ Cl$ is considerably less stable than its platinum analogue.

The Trans-Effect

The early results of work on the synthesis and reactions of square planar platinum II complexes led Chernyaev[29] in 1926 to introduce the concept of the trans-effect. He called attention to the general phenomenon that a negative ligand such as chloride has a greater labilizing effect on a group trans to it than it does on groups in cis positions. Furthermore, this labilizing effect is usually larger for a negative ligand than it is for a non π-bonding neutral group such as ammonia. Of the many definitions of this effect, perhaps the best is that given by Basolo and Pearson:[30] 'the trans-effect is the effect of a co-ordinated group upon the rate of substitution reactions of ligands opposite to it in a metal complex'. This definition implies that the trans-effect should be discussed in terms of the free-energy difference between the equilibrium state of a substrate plus nucleophile, and the activated complex. In practice, this is not easy, and it is convenient to define[16] a 'trans-influence' of a ligand as the extent to which that ligand weakens the bond trans to itself in the equilibrium state of a substrate.

Several techniques have been utilised to detect changes in Pt-X bond strengths with changes in the other ligands, particularly the group trans to X. Information on shifts in the stretching frequencies of a Pt-X bond in complexes of the type trans-A_2 Pt LX has been used[31] to assess the relative effects of different trans ligands L on the Pt-X bond strength. Using this technique Chatt and co-workers have drawn up a 'trans-effect" order H^-, $CH^-_3 > PR_3 > SbR_3 > AsR_3 > Cl^-$. Another method used to evaluate bond strength is to measure bond length directly. The hydride ligand stands high in the trans-effect series, and there is good evidence that it causes a lengthening of the Pt-X bond trans to it. The platinum-chlorine bond length in trans-$(Ph_2EtP)_2$ Pt H Cl was found[32] to be 2.42Å, which is appreciably larger than the value of 2.279Å reported[33] for the terminal Pt-Cl bond distance in $(Pr_3P)_2$ Pt_2 Cl_4. In the latter complex, the terminal chloride ligand is trans to a bridging chloride, which has a small trans-effect.

Several theories have been advanced in attempts to explain the phenomenon of the trans-effect and these are well summarised by Basolo and Pearson.[34] It appears that

ligands that are good trans activators fall in one of three categories: (1) strong σ-bonding such as H^- and CH^-_3; (2) strong π-bonding such as CO and C_2H_4; (3) moderate σ- and π-bonding such as I^-. Ligands such as NH_3 and OH^- that are weak σ and π bonders are low in the trans-effect series.

The smallness of the infra-red frequency shifts and uncertainty about the relation of n.m.r. parameters to bond strength have previously prevented characterisation of any cis-influence of ligands. Recently, however, Fryer has shown[35] that the 35 Cl n.q.r. frequency of a co-ordinated chloride group is sensitive to the nature of the cis ligands and can provide a measure of their cis-influence. The frequencies were observed for the square planar d^8 complexes trans-L_2 M Cl_2 [M = Pd, Pt] and the M-Cl bond was found to be progressively weakened in the complexes as the cis ligand L was changed, in the following order:

M = Pd PhCN < EtCN < Bu_3P < Bu_3As < pyridine < piperidine

M = Pt Bu_3P < pyridine < Me_2NH < NH_3

The cis-influence increases from left to right. A possible mechanism by which this influence can operate

has been discussed by Fryer[36], and he concluded that the principal factor determining the ^{35}Cl n.q.r. frequency for a chlorine bonded to Pt II is the Pt-Cl σ-bond order. A σ-bond mechanism of cis-influence is, therefore, indicated.

It should be noted, however, that whereas the trans-effect is critical in the chemistry of platinum II, the cis-effect is only of secondary importance.

CHAPTER ONE

REACTIONS BETWEEN COMPLEXES OF THE NICKEL GROUP AND ORGANOMERCURIALS.

CHAPTER ONE

INTRODUCTION

Preparation and properties of organomercurials

The organic derivatives of mercury are among the most stable organometallic compounds known. They are particularly noted for their inertness to oxygen and mild oxidising agents, water and weak acids. These properties contrast sharply to those of the organometallic compounds of sodium, lithium, magnesium and zinc.

The most convenient synthesis of simple organomercury compounds is to treat a mercuric halide with a Grignard reagent[37].

$$Hg\,X_2 + R\,Mg\,X \longrightarrow R\,Hg\,X + Mg\,X_2$$

$$R\,Hg\,X + R\,Mg\,X \longrightarrow R_2\,Hg + Mg\,X_2$$

By using the appropriate quantity of Grignard reagent either the organomercury halide or the symmetric diorganoderivative can be formed.

Organomercurials have been found to be useful synthetic agents and can enter into two important types of reaction[38].

(1) Replacement of the mercury in organomercury compounds under the action of free metals, resulting in organometallic complexes of the latter.

$$Ph_2\,Hg + Cd \xrightarrow[140^\circ]{\text{xylene}} Ph_2\,Cd + Hg$$

(2) Exchange with halides of metals and non-metals, resulting in a wide range of organometallic and organo-elemental compounds. This method was used to obtain the first alkyldichloro- and diarylchlorophosphines.

$$Et_2Hg + PCl_3 \longrightarrow EtPCl_2 + EtHgCl$$

$$Ph_2Hg + PhPCl_2 \longrightarrow Ph_2PCl + PhHgCl$$

Some work has been done by Heck[39] on exchange reactions between organomercurials and palladium complexes. For example, the reactive intermediate prepared from phenylmercuric chloride and palladium chloride reacts 'in situ' with ethylene to form styrene, hydrogen chloride and palladium metal.

$$PhHgCl + PdCl_2 \rightleftharpoons [PhPdCl] + HgCl_2$$

$$[PhPdCl] + CH_2 = CH_2 \longrightarrow PhCH = CH_2 + HCl + Pd$$

This reaction can be made catalytic with respect to palladium if oxidising agents such as cupric chloride are included in the reaction mixture to reoxidise elemental palladium. No intermediates could be isolated from any of these reactions.

Preparative methods for organometallic complexes of Ni,Pd,Pt

We have examined exchange reactions between organomercurials and the halides $(R_3P)_2MCl_2$ [M = Ni,Pd,Pt]

in order to prepare the organo-transition metal derivatives. The latter compounds have previously been prepared by the action of Grignard or organolithium reagents on the halide complexes.[5,19,22,23] For instance, reaction between $(Et_3 P)_2 Pd Br_2$ and a Grignard reagent, R Mg X, results in the rapid displacement of one bromide to form $(Et_3 P)_2 Pd R Br$, but a large excess is necessary to form the disubstituted derivative. Organolithium reagents are found to replace both halogens, usually quite rapidly below room temperature, and these are the preferred reagents for the preparation of dimethyl or diaryl derivatives. For the platinum complexes, organolithium reagents provide the best route to cis-diorganoplatinum compounds while the Grignard reaction normally produces the trans-monosubstituted derivative.

$$cis\text{-}(Me_2PhP)_2 PtCl_2 + 2MeLi \longrightarrow cis\text{-}(Me_2PhP)_2PtMe_2 + 2LiCl$$

$$trans\text{-}(Et_3P)_2 PtCl_2 + MeMgI \longrightarrow trans\text{-}(Et_3P)_2PtMeI + MgCl_2$$

Grignard reagents are, therefore, extremely useful in the preparation of organo-derivatives of metals particularly because of their great versatility. Parshall[40] has demonstrated this by isolating several mixed diaryl and alkyl-aryl complexes of platinum.

$$trans\text{-}(Et_3P)_2Pt(m\text{-}FC_6H_4)Cl + MeMgBr \longrightarrow trans\text{-}(Et_3P)_2PtMe(m\text{-}FC_6H_4) + MgClBr$$

$$trans\text{-}(Et_3P)_2PtPhCl + p\text{-}FC_6H_4MgBr \longrightarrow trans\text{-}(Et_3P)PtPh(p\text{-}FC_6H_4) + MgClBr$$

In some cases, however, use of Grignard reagents can lead to the formation of unexpected products. For example, Chatt and Shaw reported[23] that $cis\text{-}(Et_3P)_2PtBr_2$ and cyclohexylmagnesium bromide react to form the hydrido bromide, $(Et_3P)_2PtHBr$. The mechanism of this reaction has been examined[41] by Cross and Glockling and they conclude that two competing reaction paths are involved.

(1) $cis\text{-}(Et_3P)_2PtBr_2 + C_6H_{11}MgBr \longrightarrow (Et_3P)_2PtHBr + C_6H_{10} + MgBr_2$

$$(Et_3P)_2PtHBr \xleftarrow{H_2O} (Et_3P)_2Pt(MgBr)Br \xrightarrow{D_2O} (Et_3P)_2PtDBr$$

(2) $cis\text{-}(Et_3P)_2PtBr_2 + C_6H_{11}MgBr \longrightarrow (Et_3P)_2Pt(MgBr)Br$

Reaction (1), which accounts for 30% of the product, is independent of subsequent hydrolysis and involves formation of cyclohexene. Reaction (2), which accounts for the remaining 70% of the hydrido-platinum complex, is considered to proceed via the hydrolysis of an intermediate platinum-Grignard reagent. The evidence

for this is based on the observation that deuterolysis gives a mixture of hydrido- and deutero-platinum complexes, together with bicyclohexyl. Since reaction (2) involves halogen-metal exchange, it must produce cyclohexyl bromide which, by reaction with excess Grignard reagent, gives bicyclohexyl.

An interesting reaction which is only applicable to platinum leads to the production of halogen bridged organic derivatives of the metal.[26]

$$(Pr^n_3P)_2\ Pt_2\ X_4 + 2PhLi \longrightarrow (Pr^n_3P)_2\ Pt_2\ (Ph)_2X_2 + 2LiX \qquad [X = Br, I]$$

With platinum complexes, Grignard reagents have been shown[5] to act in a series of equilibria.

$$(Et_3P)_2\ Pt\ I_2 + Me\ Mg\ I \rightleftharpoons (Et_3P)_2\ Pt\ Me\ I + Mg\ I_2$$

$$(Et_3P)_2\ PtMeI + Me\ Mg\ I \rightleftharpoons (Et_3P)_2\ Pt\ Me_2 + Mg\ I_2$$

When $(Et_3P)_2\ PtMe_2$ and $Mg\ I_2$ are mixed in ether a precipitate is formed which rapidly redissolves, and it has been suggested that this precipitate is the six co-ordinate platinum IV intermediate $(Et_3P)_2\ Pt\ (MgI)\ Me_2I$. Oxidative addition reactions of this type, whereby complexes of metals having a d^8 electronic configuration are converted into octahedral complexes with a d^6 configuration through addition of a covalent molecule, are well known.

Thus, at 100° methyliodide is found to react with trans-$(Et_3P)_2$ Pt Me I to give the octahedral complex $(Et_3P)_2$ Pt Me_2 I_2. Also, the phenyl derivatives cis- and trans-$(Et_3P)_2$ Pt Ph_2 react with Cl_2 and I_2 to give addition compounds[5,23]. In most cases, however, the existence of octahedral platinum IV species is only transitory, and Ebsworth and co-workers have utilised H^1 n.m.r. spectroscopy to study the formation and subsequent decomposition of some six co-ordinate intermediates[42]. Their studies showed that MH_3 X [M = Si or Ge; X = Cl, Br, I] reacts with trans-$(Et_3P)_2$ Pt I_2 to yield $(Et_3P)_2$ Pt $(MH_2 X)$ (H) I_2 which slowly decomposes at room temperature to give hydrogen and trans-$(Et_3P)_2$ Pt (MHXI) I.

Because of the equilibria which operate in the Grignard reaction, this method is not ideal for the preparation of the organic derivatives. A mixture of products is often obtained, even when a large excess of reagent is employed and care must be taken at the hydrolysis stage not to displace the equilibrium.

In order to find a cleaner route to the organo-transition metal compounds we have studied the reactions between organomercurials and bisphosphine metal dihalide complexes of the nickel group, and have also considered

possible mechanisms for these reactions.

2. RESULTS OF REACTIONS BETWEEN METAL COMPLEXES AND MERCURIALS.

(a) Diaryl mercurials.

It was found that the mono-aryl complexes trans-$(R_3P)_2MR^1Cl$ [M = Ni,Pd,Pt] can be prepared by the reaction between an organomercurial, $R^1{}_2Hg$, and the appropriate metal dihalide complex.

$$cis\text{-}(Me_2PhP)_2PtCl_2 + Ph_2Hg \longrightarrow trans\text{-}(Me_2PhP)_2PtPhCl + PhHgCl$$

$$trans\text{-}(Et_3P)_2PdCl_2 + Ph_2Hg \longrightarrow trans\text{-}(Et_3P)_2PdPhCl + PhHgCl$$

$$(Ph_3P)_2NiCl_2 + (o\text{-tolyl})_2Hg \longrightarrow trans\text{-}(Ph_3P)_2Ni(o\text{-tolyl})Cl + (o\text{-tolyl})HgCl$$

The reactions are performed in refluxing ethanol and are generally complete in a few hours. Those involving the platinum and palladium complexes are clean and proceed in good yield. The nickel reaction, however, goes in poor yield, the reason for this being partly due to the instability of the product, especially in solution.

In all cases, the stereochemistry of the product is trans, as shown by n.m.r. spectroscopy, even when the starting material has the cis configuration. In this respect, the reactions resemble the action of Grignard reagents on cis-platinum halide complexes.[5] Cis-organo complexes can be prepared, however, when the starting

material is constrained to a cis-configuration by a chelating ligand such as a diphosphine or a disulphide.

$(Ph_2PCH_2PPh_2)PtCl_2 + Ph_2Hg \longrightarrow (Ph_2PCH_2PPh_2)PtPhCl + PhHgCl$

$(EtSC_2H_4SEt)PtCl_2 + Ph_2Hg \longrightarrow (EtSC_2H_4SEt)PtPhCl + PhHgCl$

Because of the insolubility of the starting platinum complexes, these reactions require a much longer reflux time than those described above. It is interesting to note that no reaction occurs between cis-$(Bu_3P)_2PtCl_2$ and Ph_2Hg when the two materials are refluxed in ethanol for 24 hours. The yellow complex, trans-$(Bu_3P)_2PtCl_2$, and unchanged Ph_2Hg were recovered from the reaction mixture. Since the reaction mixture changed from colourless to yellow on commencing the reflux, it appears that at this stage the cis-platinum complex isomerises to trans and thus prevents any reaction from taking place.

Diaryl materials were also allowed to react with halogen bridged diplatinum derivatives containing terminal phosphine and halogen groups, in an attempt to replace the terminal halogen by an organic group. Reaction between Ph_2Hg and a chloride bridged species is found to lead only to decomposition, however.

$(Et_3P)_2Pt_2Cl_4 + 2Ph_2Hg \longrightarrow$ trans-$(Et_3P)_2PtPh_2 + PhHgCl$

The products were identified by their i.r. spectrum and melting point. This reaction resembles the one

between $(Pr_3P)_2Pt_2Cl_4$ and PhLi[26] which yielded trans-$(Pr_3P)_2PtPh_2$ as the major product. Chatt and Davidson concluded from this that the required product of the reaction, $(Pr_3P)_2Pt_2Ph_2Cl_2$ was apparently unstable. This point will be discussed later. It was noted by Chatt, however, that the terminal halogen in the $(R_3P)_2Pt_2X_4$ species can be replaced, leaving the bridge intact, if X = Br or I. We also find this to be the case using organomercurials.

$$(Et_3P)_2Pt_2Br_4 + 2(o\text{-tolyl})_2Hg \longrightarrow (Et_3P)_2Pt_2(o\text{-tolyl})_2Br_2 + 2(o\text{-tolyl})\,HgBr$$

(b) Dimethyl mercury

In contrast to the reactions of Ph_2Hg with $(R_3P)_2PtCl_2$ species, the analogous Me_2Hg reactions are slow to proceed and reach completion only in pure, refluxing reagent.

$$cis\text{-}(Bu_3P)_2PtCl_2 + Me_2Hg \longrightarrow trans\text{-}(Bu_3P)_2PtMeCl + MeHgCl$$

$$cis\text{-}(Et_3P)_2PtCl_2 + Me_2Hg \longrightarrow trans\text{-}(Et_3P)_2PtMeCl + MeHgCl$$

N.m.r. spectroscopy again aided the assignment of configuration of the organo-platinum products.

In an attempt to derive more information as to the course of the organomercurial reactions, Me_2Hg was reacted with various complexes in deuterochloroform in n.m.r. tubes and spectra recorded daily. The successful reactions take

15 to 20 days at 30° to reach equilibrium, some starting material still remaining.

$$cis\text{-}(R_3P)_2PtCl_2 + Me_2Hg \longrightarrow trans\text{-}(R_3P)_2PtMeCl + MeHgCl$$

$$[R_3 = Et_3,\ Bu_3,\ Me_2Ph]$$

Those starting materials which have a trans configuration, $trans\text{-}(Et_3P)_2MCl_2$, $[M = Pd, Pt]$, show no signs of reaction after 30 days.

(c) Mercuric salts

Although the reactions between $R^1{}_2Hg$ and the metal dihalide complexes require refluxing for several hours, mercuric salts such as $HgCl_2$, HgI_2 or $Hg(CN)_2$ react rapidly at room temperature with the diorgano-metal complexes. We performed reactions between $HgCl_2$ and two diphenylplatinum complexes with the following results:

$$cis\text{-}(Et_3P)_2PtPh_2 + HgCl_2 \longrightarrow trans\text{-}(Et_3P)_2PtPhCl + PhHgCl$$

$$(EtSC_2H_4SEt)PtPh_2 + HgCl_2 \longrightarrow (EtSC_2H_4SEt)PtPhCl + PhHgCl$$

Ready cleavage of one of the platinum-carbon bonds occurs forming the monosubstituted complex. It is again pertinent to note that a trans complex is formed from a cis starting material. Reactions between mercuric salts and dimethyl-metal complexes were also performed.

$$cis\text{-}(Et_3P)_2PtMe_2 + HgI_2 \longrightarrow (Et_3P)_2PtMeI + (Et_3P)_2PtI_2 + MeHgI$$

$$cis\text{-}(Et_3P)_2PdMe_2 + HgCl_2 \longrightarrow trans\text{-}(Et_3P)_2PdCl_2 + MeHgCl$$

Immediate examination of the n.m.r. spectrum of the reactants shows that trans-$(Et_3P)_2PdMeCl$ is the initial product of the second reaction. This complex is known[15] to be relatively unstable, however, and ready cleavage of the remaining Pd-C bond occurs forming trans-$(Et_3P)_2PdCl_2$.

Some reactions of dimethylmetal compounds were examined by n.m.r. spectroscopy. The reactions between cis-$(Me_2PhP)_2PtMe_2$ and HgX_2(X = Cl, I) in particular yield interesting information.

$$\text{cis-}(Me_2PhP)_2PtMe_2 + HgX_2 \xrightarrow[CDCl_3]{\text{fast}} \text{cis-}(Me_2PhP)_2PtMeX + (Me_2PhP)_2PtX_2 + Me_2Hg + MeHgX$$

$$\downarrow \begin{matrix} \text{slow } X = Cl \\ \text{fast } X = I \end{matrix}$$

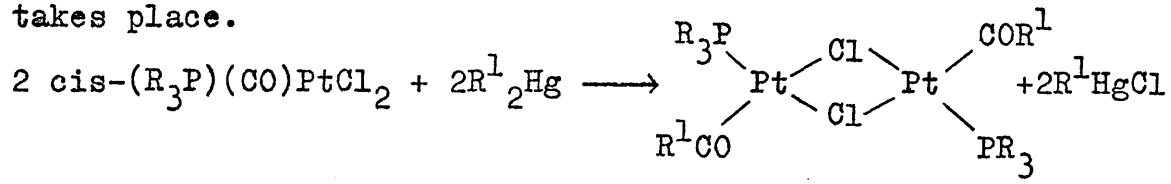
$$\text{trans-}(Me_2PhP)_2PtMeX$$

The cis-monosubstituted complex isomerises to the trans-derivative within 1 hour for X = I, but when X = Cl the process requires 2 days. Other reactions which we examined by this method include $HgCl_2$ with $(Me_2PC_2H_4PMe_2)PtMe_2$, $(Ph_2PCH_2PPh_2)PtMe_2$ and $(Et_3P)_2PdMe_2$ and cis-$(Ph_3P)_2PtMe_2$ with $HgCl_2$ and $Hg(CN)_2$. In all these cases resonances due to Me_2Hg and MeHgX [X = Cl, I, CN] are detected.

(d) <u>cis-$(R_3P)(CO)PtCl_2$ and organomercurials</u>

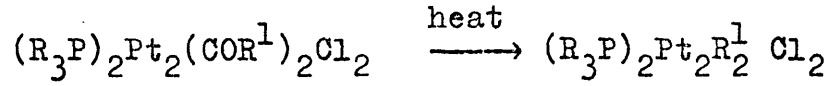
Exchange reactions are observed between organomercurials

and carbonyl complexes of the type cis-$(R_3P)(CO)PtCl_2$. However, instead of formation of the $(R_3P)(CO)PtR^1Cl$ compounds, carbonyl insertion into the Pt-C bond takes place.



(R = Bu, Ph; R^1 = Me, Ph)

These reactions are complete after a few hours at room temperature, diphenylmercury reacting slightly more readily than dimethylmercury. Final traces of the organomercuric by-product can only be removed by vacuum sublimation ca.80°/0.05m.m. Hg, and complete purification of the acyl complexes is, therefore, difficult since prolonged heating causes loss of carbon monoxide.



The loss of carbon monoxide on heating is a common reaction of metal acyls and has been observed[27] in mononuclear platinum compounds such as trans-$(Et_3P)_2Pt(COR)Cl$.

Halogen-bridged binuclear acetyl and benzoyl complexes of this type have not previously been described. With the exception of $(Bu_3P)_2Pt_2(COMe)_2Cl_2$ which we could obtain only as an oil, they are crystalline solids which decompose below their melting points. The compounds were

characterised by i.r., n.m.r. and mass spectroscopy, and elemental analysis. Bridge-splitting reactions with C_5H_5Tl and R_3^2P, to form $(\pi\text{-}C_5H_5)(R_3P)Pt(COR^1)$ and trans-$(R_3P)(R_3^2P)Pt(COR^1)Cl$ respectively, also aided characterisation.

In view of the novel compounds produced by reacting organomercurials with cis-$(R_3P)(CO)PtCl_2$ complexes, we were interested to determine whether similar derivatives could be formed if organolithium or Grignard reagents were used in place of organomercurials. We observe that reaction with methyl lithium fails to produce any insertion compounds. Thus, reaction between equimolar amounts of $(R_3P)(CO)PtCl_2$ and MeLi yields a mixture of compounds showing three stretching frequencies in the i.r. spectrum associated with terminal carbonyl groups. It is probable that a mixture of $(Ph_3P)(CO)PtMe_2$, $(Ph_3P)(CO)PtMeCl$ and $(Ph_3P)(CO)PtCl_2$ is present. When cis-$(Bu_3P)(CO)PtCl_2$ is reacted with an excess of methyl lithium, the oil produced shows only one carbonyl frequency, indicating formation of $(Bu_3P)(CO)PtMe_2$. The reaction between $(Bu_3P)(CO)PtCl_2$ and excess phenyl magnesium bromide is more complicated and is accompanied by decomposition. Treatment of the crude oil, obtained from the reaction, with light-petroleum causes precipitation of the carbonyl

insertion complex $(Bu_3P)_2Pt_2(COPh)_2Br_2$. The i.r. spectrum of the oily residue shows the presence of species with terminal carbonyl groups. Benzophenone is also produced. Thus, it appears that the Grignard reaction produces both normal substitution products and insertion products.

A reaction between Vaska's compound, trans-$(Ph_3P)_2(CO)IrCl$, and Ph_2Hg was performed in an attempt to elucidate the reaction mechanism involved in the platinum systems (vide ultra). The reaction time was 24 hours, at room temperature in benzene, and the i.r. spectrum of the solid obtained on removal of solvent indicates that oxidative addition of Ph_2Hg to the iridium I species has taken place.

$$\text{trans-}(Ph_3P)_2(CO)IrCl + Ph_2Hg \longrightarrow (Ph_3P)_2(CO)ClIr(HgPh)Ph$$

Satisfactory analytical data are lacking for this complex. The i.r. spectrum, however, provides good evidence that the formulation of the product is correct, since (a) ν(CO) increases from the starting material to the product, indicating that oxidation of Ir I to Ir III has occurred; (b) ν(Ir-Cl) of the product is in the correct position for a chloride group trans to CO in an octahedral Ir III complex (vide ultra) and (c) no phenylmercuric chloride or mercuric chloride is detected.

3. DISCUSSION.

It is interesting to note that, for mononuclear complexes with monodentate ligands, the trans-isomer is usually produced regardless of the stereochemistry of the starting material.

$$cis\text{-}(R_3P)_2MCl_2 + R^1{}_2Hg \longrightarrow trans\text{-}(R_3P)_2MR^1Cl + R^1HgCl$$

In this respect the organomercurial reactions resemble those of Grignard reagents. A further point of similarity is found in the comparison of phenyl and methyl reagents. With the mercurials, the methyl reaction proceeds more slowly than the corresponding phenyl one. Similarly, a large excess of methyl Grignard reagent is necessary to produce good yields of $trans\text{-}(Et_3P)_2PtMeI$, but the reaction of phenylmagnesium bromide with $(Et_3P)_2PtCl_2$ can give diphenylplatinum derivatives. These reactions may reflect a greater stability of phenylplatinum complexes.

Very recently, Italian workers have reported that mercuric chloride cleaves the Pt-Ph bond of $(C_{10}H_{12}oMe)(Ph_3P)PtPh$ to produce $(C_{10}H_{12}oMe)(Ph_3P)PtCl$ and $PhHgCl$[43]. Thus, it appears that reaction between mercuric salts and organoplatinum complexes is a general method of cleaving platinum-carbon σ-bonds.

Similar forward and back reactions to those which we observe have been demonstrated where silylmercury

and germylmercury compounds replace diaryl- or dialkylmercurials[44,45], but these are complicated by the decomposition of the mercury by-product.

$$cis\text{-}(Et_3P)_2PtCl_2 + (Me_3Si)_2Hg \longrightarrow trans\text{-}(Et_3P)_2Pt(SiMe_3)Cl + Me_3SiCl + Hg$$

The mercurial reactions are most likely to proceed by one of two mechanisms.

I. Oxidative addition to platinum IV intermediates.

$$(Bu_3P)_2PtCl_2 + Me_2Hg \longrightarrow (Bu_3P)_2Cl_2Pt(HgMe)Me \longrightarrow products$$

Oxidative addition reactions, whereby complexes of metals having a d^8 electronic configuration are converted into octahedral complexes having a d^6 configuration through addition of a covalent molecule, are well established (see reference 35 for examples). The tendency for d^8 complexes to undergo oxidative additions depends markedly on the nature of the central metal ion and the ligands attached to it. Nyholm has considered[46] three energy quantities which are important in the oxidation process, and if we consider the d^8 complex to be oxidised by a mercurial, these quantities are:

(a) Promotion of the d^8 atom, in the square complex, from the $nd_\epsilon^6\ nd^2{}_z2$ to the $nd_\epsilon^6\ nd_z2\ (n+1)p$ configuration.

This increases rapidly with formal charge.

(b) The dissociation energy of the RHg-R bond.

(c) The energy of formation of the two bonds to the metal atom, M-HgR and M-R. These are expected to increase in strength as the formal charge rises, but not so rapidly as does the increase in promotion energy.

As a consequence of (a), the ease with which the $M^{x} \longrightarrow M^{x+2}$ valency change occurs for the sequencies Os^{o}, Ir^{I}, Pt^{II} and Au^{III} is highly sensitive to the initial valency. Thus, the $Au^{III} \longrightarrow Au^{V}$ oxidation is unknown. Platinum II compounds can be oxidised to platinum IV derivatives by halogens and methyl iodide, for example.

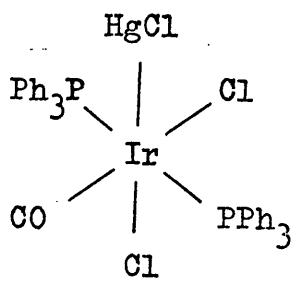
$$trans\text{-}(Et_3P)_2PtMeI + MeI \longrightarrow (Et_3P)_2PtMe_2I_2$$

Also, the reaction of $HgCl_2$ and $(Et_3P)_2Pt(GePh_3)_2$ gave some evidence[45] for a Pt-Hg intermediate which could have been produced by elimination of Ph_3GeCl from $(Et_3P)_2Pt(GePh_3)_2Cl(HgCl)$.

The $Ir^{I} \longrightarrow Ir^{III}$ oxidation is much more easily effected, Vaska's compound, $trans\text{-}(Ph_3P)_2(CO)IrCl$, being oxidised by species such as oxygen, hydrogen, halogens, hydrogen halides, metal halides and allyl halides[47]

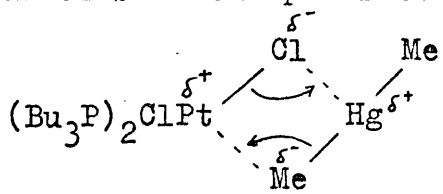
In connection with this work, the most interesting reaction of Vaska's compound is that with $HgCl_2$[46]

$$trans\text{-}(Ph_3P)_2(CO)IrCl + HgCl_2 \longrightarrow$$



II. Bimolecular electrophilic substitution.

The second possible mechanism for the mercurial reactions involves bimolecular electrophilic substitution. In the internal electrophilic substitution mechanism (SEi) a four-centred cyclic transition state is formed by concurrent attack of the two ends of the reagent upon the extremities of the polarised platinum-chlorine bond.

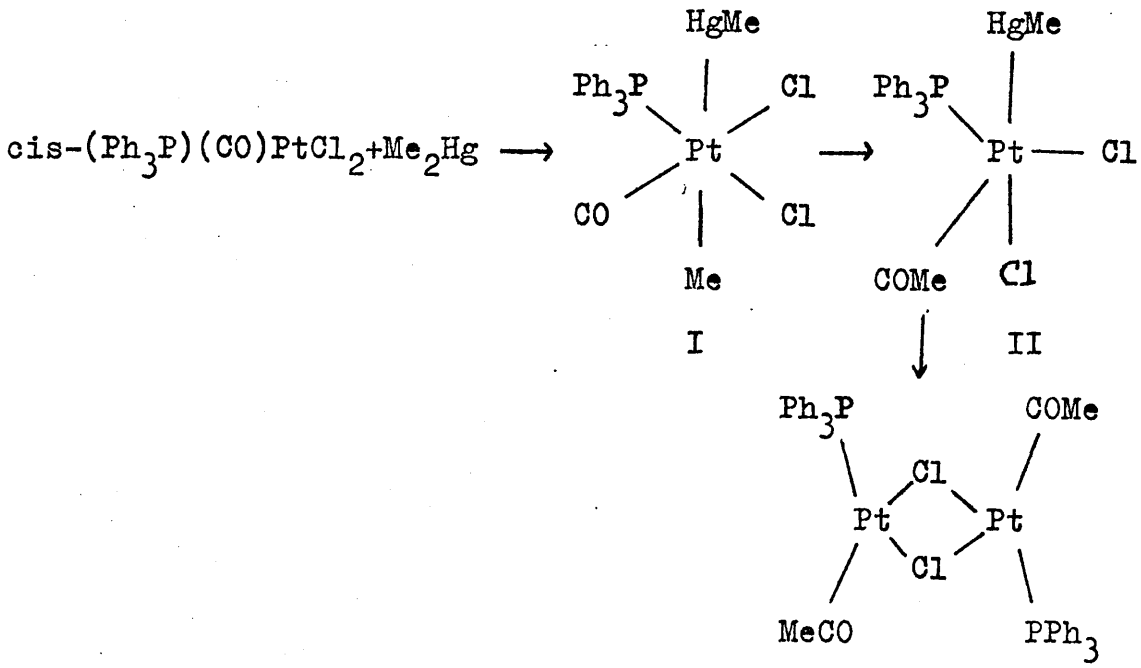


This type of reaction is common in mercury substitutions. If the carbonyl reactions are considered first, the different reaction products of methyl lithium and organomercurials with phosphine carbonyl platinum halide complexes indicate that the reactions proceed by different routes. The reaction with excess methyl lithium produces

the species $(R_3P)(CO)PtMe_2$ possibly by attack of the methyl carbanion at platinum, a situation similar to route II above. If the organomercurial reaction also proceeded by this mechanism, the derivative $(R_3P)(CO)PtR^1Cl$ should be formed. Since this is not the case, it is postulated that the first stage of this reaction involves formation of the platinum IV octahedral intermediate, $(R_3P)(CO)Cl_2Pt(HgR^1)R^1$. This hypothesis is supported by our finding that Ph_2Hg, like $HgCl_2$, oxidises Vaska's complex to yield $(Ph_3P)_2(CO)ClIr(HgPh)Ph$.

The metal-carbonyl bond in these octahedral complexes isweaker than that in the square-planar starting materials since the oxidation state of the metal is now higher and less back donation into empty antibonding orbitals of the CO ligand is possible. Evidence for this is obtained by comparing carbonyl stretching frequencies of the iridium compounds, $\nu(CO)$ of trans-$(Ph_3P)_2(CO)IrCl$ being 1955cm^{-1} whereas $\nu(CO)$ of $(Ph_3P)_2(CO)ClIr(HgPh)Ph$ is 2000cm^{-1}. The effect will be even more pronounced in going from platinum II to platinum IV. The weak platinum-carbonyl bond in the platinum IV complex, $(R_3P)(CO)Cl_2Pt(HgR^1)R^1$ may enhance CO group insertion into the platinum-R^1 bond forming the five-coordinate species $(R_3P)(COR^1)Cl_2Pt(HgR^1)$ which then eliminates R^1HgCl.

The reaction scheme is, therefore, of the form



The stereochemistry of I and II are uncertain, that of I depending on whether $HgMe_2$ adds cis or trans. Five co-ordinate species are also thought to be involved as intermediates in the carbonylation of $(R_3P)_2PtRCl$ complexes[27]. Some further evidence for the oxidative addition mechanism is provided by the fact that the reaction between excess Grignard reagent, PhMhBr, and $(Bu_3P)(CO)PtCl_2$ produces both the normal substitution product $(Bu_3P)(CO)PtPh_2$ and a small amount of the insertion complex $(Bu_3P)_2Pt_2(COPh)_2Br_2$.

Grignard reagents normally act bycarbanion attack at the metal[19],

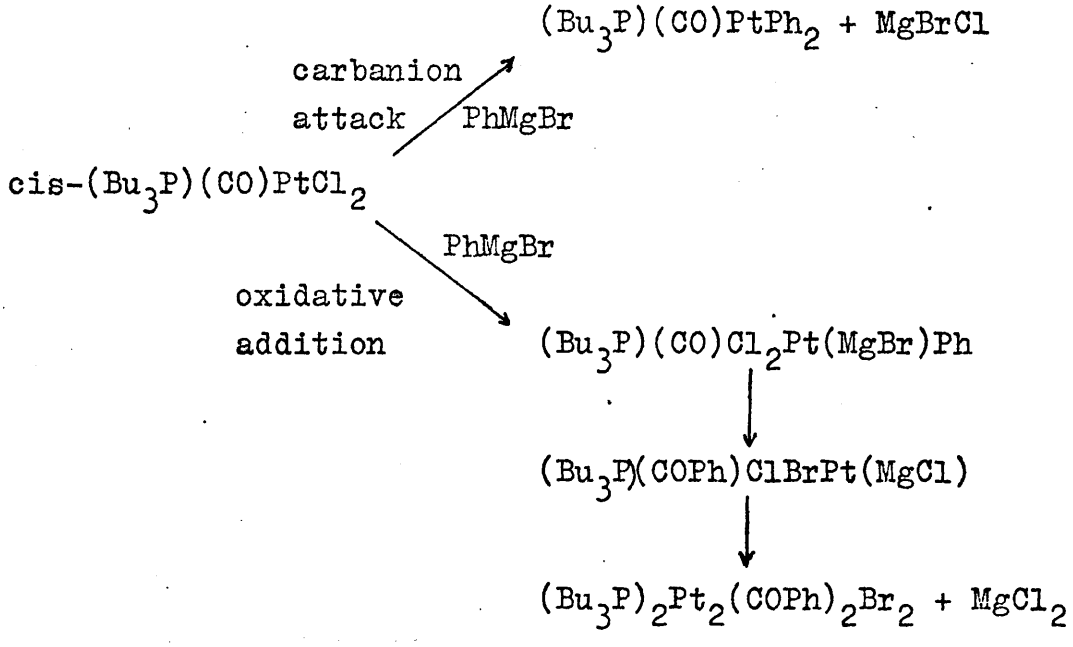
trans-$(Et_2PhP)_2NiBr_2$+(mesityl)MgBr ⟶ trans-$(Et_2PhP)_2$Ni-(mesityl)$_2$+ $MgBr_2$

In this reaction there is no tendency for the reverse reaction to occur perhaps because of steric hindrance. In contrast, MgI_2 reacts with $(Ph_3P)_2PtMe_2$,

$$cis\text{-}(Ph_3P)_2PtMe_2 + MgI_2 \longrightarrow trans\text{-}(Ph_3P)_2PtMeI + MeMgI$$

and Chatt and Shaw have evidence[5] that this reaction proceeds via a platinum IV species $(Ph_3P)_2Me_2Pt(MgI)I$. Cross and Glockling have also postulated[41] that a platinum-Grignard reagent is formed as an intermediate in the reaction between $C_6H_{11}MgBr$ and $(Et_3P)_2PtBr_2$,

Both mechanisms may be involved in the reaction between PhMgBr and $(Bu_3P)(CO)PtCl_2$



The production of the chloride bridged species

$(R_3P)_2Pt_2(COR^1)_2Cl_2$ from the mercurial reactions is interesting since the analogous phenyl complexes $(R_3P)_2Pt_2Ph_2X_2$ are known only for X = Br or I. Chatt and Davidson concluded[26] from this that the chloride bridged derivatives were 'apparently unstable'. The trans influence of the acetyl or benzoyl group, however, is as great, if not greater, than that of the phenyl ligand as demonstrated by the fact that we observe ν(Pt-Cl) in trans-$(Et_3P)_2Pt(COPh)Cl$ at 252cm^{-1}, whereas in trans-$(Et_3P)_2PtPhCl$ ν(Pt-Cl) is at 270cm^{-1}. That is, the platinum-chlorine bond is slightly weaker when the benzoyl group is trans than when the phenyl group is trans. There is, therefore, apparently no reason why the complex $(R_3P)_2Pt_2Ph_2Cl_2$ should not be at least as stable as its benzoyl analogue, and in fact we find on heating the compound $(Ph_3P)_2Pt_2(COPh)_2Cl_2$ under vacuum that CO can be eliminated to form the phenyl derivative. It must be assumed that in the reactions between PhMgBr, PhLi or Ph_2Hg and $(R_3P)_2Pt_2Cl_4$ unstable intermediates are formed at some stage which decompose to yield trans-$(R_3P)_2PtPh_2$ rather than form the required complex.

The mechanism of the reactions between the

bis-phosphine metal complexes and organomercurials cannot be determined as certainly as can that of the reactions in which phosphine carbonyl compounds are involved. It would appear that the oxidative addition mechanism does not operate in the reaction of $(Ph_3P)_2NiCl_2$ and $(o\text{-tolyl})_2Hg$ since nickel II complexes show no tendency to be oxidised to Ni IV. For example, there is no reaction observed[19] after 2 days when MgI_2 is added to trans-$(Et_2PhP)_2Ni(mesityl)_2$. No direct evidence is available as to the mechanism operating for the platinum compounds, although we tend to favour the oxidative addition route.

The fact that the reaction of cis-$)R_3P)_2PtCl_2$ and Me_2Hg is slow whereas the reverse reaction between cis-$(R_3P)_2PtMe_2$ and $HgCl_2$ is fast indicates that a series of equilibria are operating, the equilibrium of the system lying well to the left.

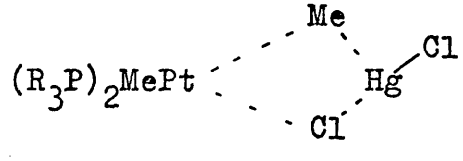
$$\begin{array}{ccc} & \overset{Me_2Hg}{\underset{slow}{\rightleftharpoons}} & \\ cis\text{-}(R_3P)_2P{+}Cl_2 & & trans\text{-}(R_3P)_2PtMeCl \\ & \underset{HgCl_2}{\overset{fast}{\rightleftharpoons}} & \uparrow \text{slow} \\ & \overset{HgCl_2}{\underset{slow}{\rightleftharpoons}} & \\ cis\text{-}(R_3P)_2PtMe_2 & \underset{Me_2Hg}{\overset{fast}{\rightleftharpoons}} & cis\text{-}(R_3P)_2PtMeCl \end{array}$$

One of the factors influencing the ability of a complex to undergo an oxidative addition reaction is, as we described, the energy required to promote an electron from the nd_{z^2} orbital to the (n+1)p orbital. This energy quantity decreases with the formal charge on the metal. The charge on the platinum atom in cis-$(R_3P)_2PtMe_2$ will be less than that in the complex cis-$(R_3P)_2PtCl_2$ since the methyl group is a much better donor ligand than chloride. Therefore, neglecting other considerations, cis-$(R_3P)_2PtMe_2$ will undergo oxidative additions much more readily than cis-$(R_3P)_2PtCl_2$, and consequently reactions involving cis-$(R_3P)_2PtMe_2$ should be faster.

Some evidence for this is provided by the work of Chatt and Shaw who observed[5] that methyl iodide forms a six coordinate platinum IV species with trans-$(Et_3P)_2PtMeI$ but does not react with trans-$(Et_3P)_2PtI_2$. Since the charge on platinum is less in the latter complex, this also suggests that electrophilic attack at platinum is important in the rate determining step. Similar reasoning has been used[42] to account for the slowness of reactions of trans-$(Et_3P)_2PtCl_2$with MH_3X [M = Si, Ge; X = Cl, Br, I] compared with those of trans-$(Et_3P)_2PtI_2$.

Energy factors (b) and (c) described previously must also be examined since they will affect the rate and course of reaction. The energies required to break the LHg-L bond (L = Me,Cl) are known to be 81 K.cal./mole for $CH_3Hg - CH_3$ and 52 k.cal./mole for ClHg - Cl, but unfortunately sufficient information is not available for the platinum system for any quantitative assessment to be made of the relative energies of the cis-$(R_3P)_2PtMe_2/HgCl_2$ and cis-$(R_3P)_2PtCl_2/HgMe_2$ systems. Nevertheless, we consider that the vast difference in rate between the two reaction systems may be explained by postulating that the cis-$(R_3P)PtCl_2/HgMe_2$ combination has a lower ground state energy than cis-$(R_3P)_2PtMe_2/HgCl_2$.

Kinetic factors must be considered to determine which mechanism operates, the mechanism depending on which route, oxidative addition or bimolecular electrophilic substitution, leads to the lower energy activated complexes. Unfortunately, it is not possible to even qualitatively assess which of the two states $(R_3P)_2Me_2Pt(HgCl)Cl$ or



involves the lower energy requirement. It is interesting to note, however, that the polarity of the solvent does

not influence the rate of reaction, the reactions being equally fast in benzene or chloroform. If the electrophilic substitution mechanism operates, the reactions would be expected to be accelerated by a polar solvent, which could lower the energy of the 4-centred activated complex. This observation is, therefore, tenuous avidence for the oxidative addition route.

Finally, the fact that trans-$(Et_3P)_2PtCl_2$, unlike its cis-isomer, fails to react with Me_2Hg, is worthy of comment. The explanation may be that the Pt-Cl bond in the trans complex, being trans to chlorine, is stronger than that in the cis complex in which it is trans to phosphorus, and thus is more difficult to replace.

4. SPECTROSCOPIC EXAMINATION OF COMPLEXES

(a) Nuclear Magnetic Resonance

Nuclear magnetic resonance spectroscopy has found wide use in the solution of chemical problems, including numerous applications to the study of organometallic compounds of the nickel group. In particular, when the metal atom has one or more phosphine groups bonded to it, an examination of the resonance pattern due to organic groups which couple to ^{31}P ($I = \frac{1}{2}$, abundance 100%) can yield valuable structural information. Shaw and co-workers have exploited this technique in the study of some dimethylphenylphosphine complexes of Ni[49], Pd and Pt[50,51]. The palladium and platinum complexes they examined were of the form cis- and trans-$(Me_2PhP)_2MX_2$ [M = Pd, Pt; X = Cl, Br, I]. The methyl resonance for the cis-palladium compounds was found to consist of a symmetrical 1:1 doublet, due to coupling of the methyl groups to ^{31}P, J(P-H) ca.10Hz. The spectra of the cis-platinum compounds were more complicated, consisting of three doublets, since 33% of naturally occurring platinum consists of the ^{195}Pt isotope of nuclear spin $\frac{1}{2}$. The observed methyl resonance pattern is, therefore, made up of a central doublet of relative intensity 4 due to

phosphines complexed to other platinum isotopes, and two satellite doublets each of relative intensity 1 from phosphines complexed to ^{195}Pt, J(Pt-H) ca.35Hz.

The spectra of the trans complexes do not show a doublet for the methyl resonance but rather a 1:2:1 triplet, the separation between the outer lines of the triplet being J(P-H) ca.8Hz. This phenomenon is known as 'virtual coupling'. The spectra of the trans-platinum compounds show, in addition, coupling to ^{195}Pt, J(Pt-H) ca.27Hz. Series of nickel complexes of the type $(Me_2PhP)_2$ NiXR [R = o-tolyl, 1-naphthyl][49] and $(Me_2PhP)_2$ NiMeR^1 [R^1 = C_6Cl_5, mesityl, C_6F_5][52] have also been studied by n.m.r. spectroscopy, and were found to exhibit virtual coupling thus showing that they have a trans configuration. Other examples where virtual coupling has been utilised to assign stereochemistry include n.m.r. studies on the adducts formed from the reactions in solution of planar-iridium I complexes with a variety of reagents[47].

The phenomenon of virtual coupling has been explained by Harris[53] who has examined spectra of the $XnAA^1Xn^1$ type in some detail, subject to three limitations: (i) only expressions for resonances of the X nucleus were presented, (ii) it was assumed that coupling Jx

between nuclei of types X and X^1 was zero, and (iii) only nuclei of spin $\frac{1}{2}$ were considered. The X spectrum calculated for this system was then found to consist of a doublet, contributing to half the total intensity, of separation $N = |J_{AX} + J_{AX^1}|$ and n sets of 4 lines symmetric about the centre of the X pattern. Each set of lines is characterised by a parameter χ, which takes values from 1 to n. Usually the inner pair of lines of each set is sufficiently intense to be observed but the only outer pair to be seen is that of the $\chi = 1$ set. This general description may be considerably simplified in certain cases, and there are two extreme types.
(a) $|J_A| \gg L = |J_{AX} - J_{AX^1}|$ giving approximately an A_2X_{2n} spectrum. In this case the outer lines have negligible intensity and the inner lines fall very close to ν_X. The whole X spectrum, therefore, has the appearance of a 1:2:1 triplet, the separation between the outer lines being N. The spectra of the complexes trans-$(Me_2PhP)_2MX_2$ [M = Pd,Pt], of the $H_6PP^1H_6^1$ type, are examples of this limiting case. The two phosphorus atoms in trans positions couple very strongly with the effect that $J(PP^1) \gg |J_{PH} - J_{PH^1}|$. The characteristic methyl resonance pattern for a trans-platinum compound,

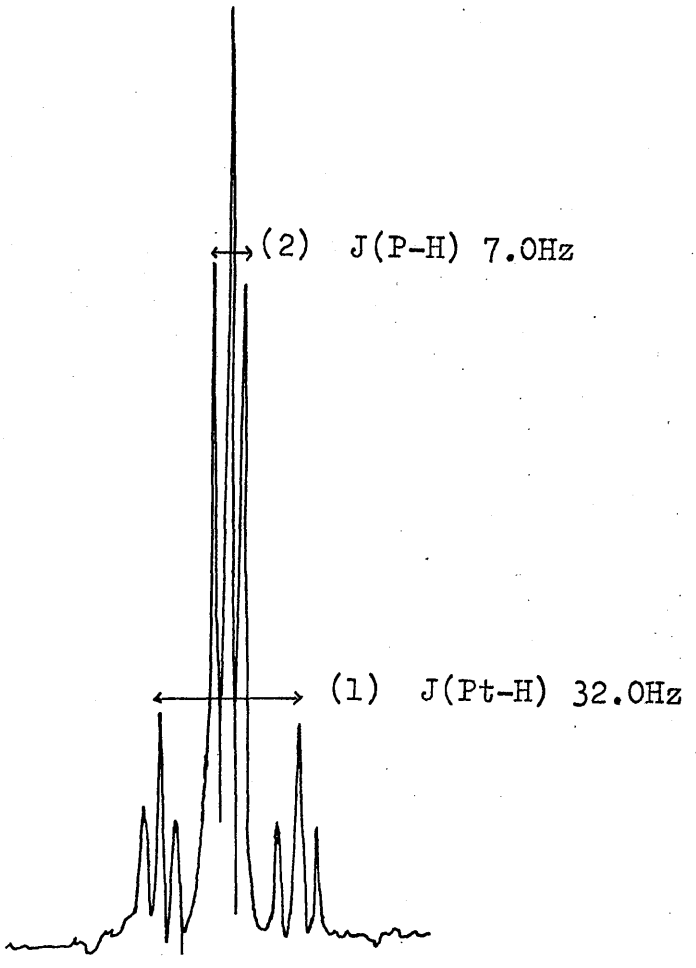
trans-$(Me_2PhP)_2PtPhCl$ is shown in figure 4(a).

(b) $JA \longrightarrow 0$, giving approximately an XnAM spectrum. In this case the whole X spectrum consists of four lines with spacings N and L. The complexes, cis-$(Me_2PhP)_2MX_2$, are examples of this limiting case, since $J(PP^1)$ is very small. Also, since the 'long range' coupling constant $J(P^1H)$ is very small, <1Hz, L is equal to N and the methyl resonance, therefore, consists solely of a 1:1 doublet. Satellite doublets are observed for the platinum compounds, and the methyl region of cis-$(Me_2PhP)_2PtCl_2$ is shown in figure 4(b).

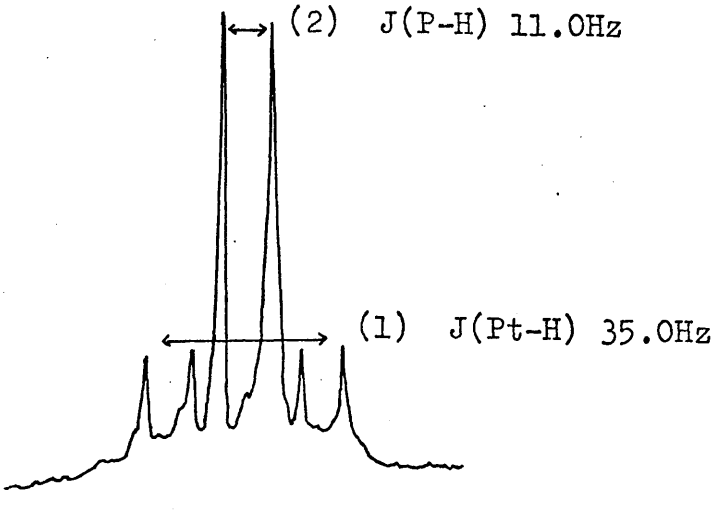
We have employed n.m.r. spectroscopy not only as a means of assigning stereochemistry to reaction products but also as a means of following the course of the reactions.

I. Metal-phenyl complexes.

N.m.r. parameters for both the complexes $(R_3P)_2MCl_2$ (R_3 = Et_3, Me_2Ph; M = Pd,Pt) and their reaction products with Ph_2Hg are listed in table 1. The methyl resonance for the complex cis-$(Me_2PhP)_2PtCl_2$ consists of 3 doublets of relative intensity 1:4:1 centred at 8.23τ, J(P-H) 11.0Hz, J(Pt-H) 35.0Hz. The reaction



(a) Methyl region of trans-$(Me_2PhP)_2PtPhCl$ centred at τ 8.51



(b) Methyl region of cis-$(Me_2PhP)_2PtCl_2$ centred at τ 8.23

FIGURE 4.

TABLE 1

N.m.r. data for metal complexes.

COMPLEX	τ ($C\underline{H}_3$-CH_2-P)	τ (CH_3-$C\underline{H}_2$-P)	τ (C_6H_5)	J($\underline{C}H_3$-CH_2-$\underline{P}$)Hz	J(Pt-H)Hz
trans-$(Et_3P)_2PdCl_2$	8.83	8.17		15.0	
trans-$(Et_3P)_2PdPhCl$	8.93	8.53	3.15	14.0	
cis-$(Me_2PhP)_2PtCl_2$	8.23			11.0	35.0
trans-$(Me_2PhP)_2PtPhCl$	8.51		3.20	7.0	32.0
$[(Ph_2PC_2H_4PPh_2)(PEt_3)PtPh]^+Cl^-$	8.90		3.18	18.0	

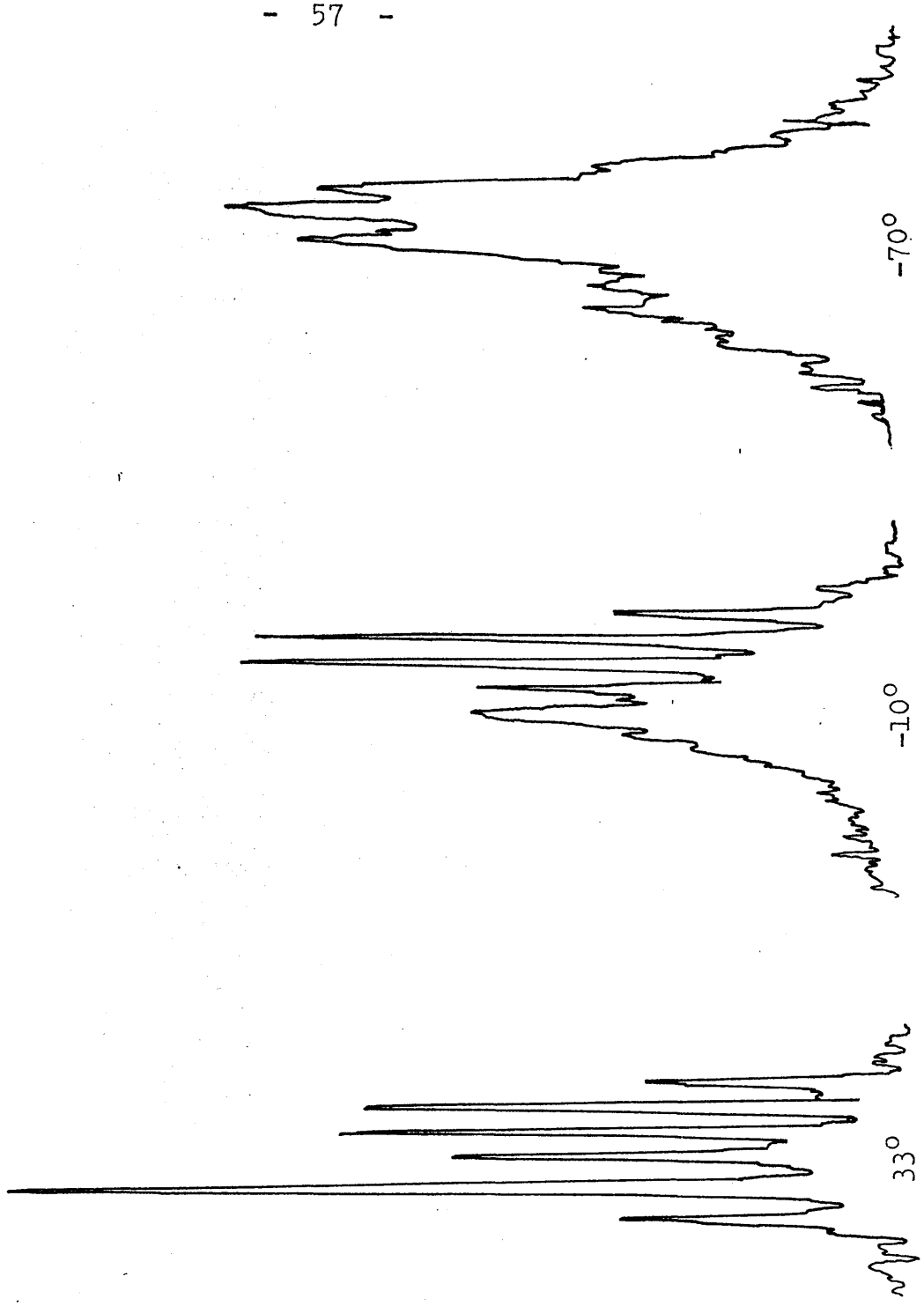
All spectra were recorded in $CDCl_3$

product $(Me_2PhP)_2PtPhCl$ shows a methyl resonance of 3 triplets, showing virtual coupling of trans phosphorus atoms, centred at 8.51τ , J(P-H)7.0Hz, J(Pt-H)32.0Hz. A multiplet centred at 3.20τ , associated with the phenyl protons, was also observed. The methyl region of the spectra of these two complexes is shown in figure 4.

The trans compounds $(Et_3P)_2PdCl_2$ and $(Et_3P)_2PdPhCl$ exhibit a more complicated spectrum in the methyl region. The methyl protons of the ethyl group couple to the methylene protons, giving rise to a 1:2:1 triplet $J(CH_3\text{-}CH_2)$ca.7Hz. Coupling to the ^{31}P nucleus then occurs, J(P-H)ca.14Hz , resulting in two 1:2:1 triplets. The spectrum is further complicated by the phosphorus atoms being in a trans configuration and a 2:4:2 triplet results between the other triplets. Overlap between the centre lines of the smaller triplets with the outer lines of the larger one, and between the centre line of the larger triplet and the inner lines of the smaller ones leads to the observed 1:4:6:4:1 pattern. In the methylene region of the spectra at least 13 lines are detected. In the phenyl compound, the resonances due to the aromatic protons are again centred at 3.15τ .

The n.m.r. spectrum of the reaction product between trans-$(Et_3P)_2PtPhCl$ and $Ph_2PC_2H_4PPh_2$ proved useful in determining the constitution of the compound. The observed elemental analysis figures for the carbon and hydrogen percentages were too high if the complex were formulated as $[(Ph_2PC_2H_4PPh_2)(PEt_3)PtPh]^+Cl^-$, but were correct if a molecule of benzene of solvation was added to the formula. Integration of the n.m.r. spectrum gives a ratio of aromatic to aliphatic protons of 31:19 which is correct for $[(Ph_2PC_2H_4PPh_2)(PEt_3)PtPh]^+Cl^-.\ C_6H_6$

The room temperature spectrum observed for the chelating sulphide complex $(EtSC_2H_4SEt)PtPh_2$ led us to investigate its spectrum at low temperature and also the spectra of similar compounds. At room temperature, the n.m.r. spectrum consists of a singlet from the bridging SC_2H_4S unit, with satellite peaks due to coupling with ^{195}Pt, J(Pt-H)20Hz, and a 1:3:3:1 quartet from the methylenes of the terminal ethyl groups, with satellite quartets, J(Pt-H)16Hz. On cooling a solution of the material in $CDCl_3/CF_2Cl_2$ to ca.-90° a complex resonance pattern is observed for the methylene groups bonded to sulphur. The spectra of the methylene region, at various temperatures, are shown in figure 5.



Methylene region of $(EtSC_2H_4SEt)PtPh_2$ at various temperatures.

FIGURE 5.

The pyramidal nature of sulphur in this type of complex is now well established and recent ^{1}H n.m.r. work on a number of thioether derivatives of platinum II shows that at high temperatures, inversion of sulphur becomes rapid and the pyramidal configurations average to a 'planar' situation[54].

We can, therefore, rationalise our observations by suggesting that the complex pattern in the methylene region at low temperatures is due to the methylene groups being bonded to sulphur atoms in asymmetric environments. As the temperature is raised the methylene resonances coalesce as inversion becomes rapid and finally at room temperature a simple pattern due to an average 'planar' C_2SPt configuration emerges.

We were interested in determining whether the inversion rate at sulphur was dependent on the trans ligand X, and the work was extended[55] to include variable temperature n.m.r. measurements on a series of complexes $(RSC_2H_4SR)MX_2$ (R = n-Bu, n-Pr, Et; M = Pd,Pt; X = Cl,Br,I). The results are summarised in table 2, which lists the values of the resonances of the methylenes bonded to sulphur and the coalescence temperatures. A marked difference in coalescence temperature is apparent as X^-

TABLE 2 ^{1}H n.m.r. data for $(RSC_2H_4SR)MX_2$ complexes[a]

COMPOUND	COALESCENCE TEMPERATURE (°C)	HIGH-TEMPERATURE AVERAGED SPECTRA				
		TEMP.(°C)	τ SC_2H_4S	(J Pt-H)Hz	τ SCH_2R	(J Pt-H)Hz
$(BuSC_2H_4SBu)PtCl_2$	95[b]	137	7.01[d]	49	6.83[c]	30
$(BuSC_2H_4SBu)PtBr_2$	75[b]	127	7.01[d]	49	6.76[c]	30
$(BuSC_2H_4SBu)PtI_2$	57[b,c]	107[b]	7.12[d]	48	6.81[c]	24
$PrSC_2H_4SPr)$ $PtCl_2$	95[b]	155	7.09[d]	47	6.90[c]	32
$(PrSC_2H_4SPr)PtBr_2$	70[b]	120	7.06[d]	46	6.85[c]	32
$(PrSC_2H_4SPr)PtI_2$	50[b]	120	7.16[d]	45	6.84[c]	26
$(EtSC_2H_4SEt)PtCl_2$	85[b]	155	7.09[d]	46	6.84[f]	30
$(EtSC_2H_4SEt)PtI_2$	50[b,c]	125[b]	7.16[d]	48	6.76[f]	30
$(EtSC_2H_4SEt)PtPh_2$	-70[c]	35	7.42[d]	20	7.55[f]	16
$(BuSC_2H_4SBu)PdCl_2$	50[c]	80	6.87[g]		6.77[h]	
$(BuSC_2H_4SBu)PdBr_2$	35[c]	70	6.89[g]		6.73[h]	
$(BuSC_2H_4SBu)PdI_2$	0[c]	50	7.00[g]		6.74[h]	

(a) measured at 100MHz; (b) in $PhNO_2$; (c) in $CDCl_3$; (d) singlet with ^{195}Pt satellites; (e) triplet with ^{195}Pt satellites; (f) quartet with ^{195}Pt satellites; (g) singlet; (h) triplet

changes from Cl^- to Br^- to I^- to Ph^-. As the trans-influence increases in the order $Cl^- < Br^- < I^- < Ph^-$ for palladium and platinum compounds, the increase in the inversion rate at sulphur in this order probably reflects weaker metal-sulphur bond strengths. The method is novel and may have extensions in trans-effect transmission in square-planar complexes of metals in this part of the periodic table.

Finally, in this section, the position of the peaks associated with the phenyl group, in the platinum and palladium compounds discussed, is worthy of note. In all cases, a multiplet centred at about 3.2τ is observed. This value is rather high and suggests that as in aniline, for example, shielding of the ring protons is occurring. In this case, one can envisage back-donation from d orbitals on the metal into appropriate orbitals of the benzene ring. Evidence for this is that in organo-metallic complexes in which no back-donation is possible, the aromatic resonances are close to that of benzene itself. Thus, Ph_2Hg and PhHgCl, in which the mercury bonding orbitals are probably sp hybrids, have peaks at 2.64τ and 2.65τ respectively.

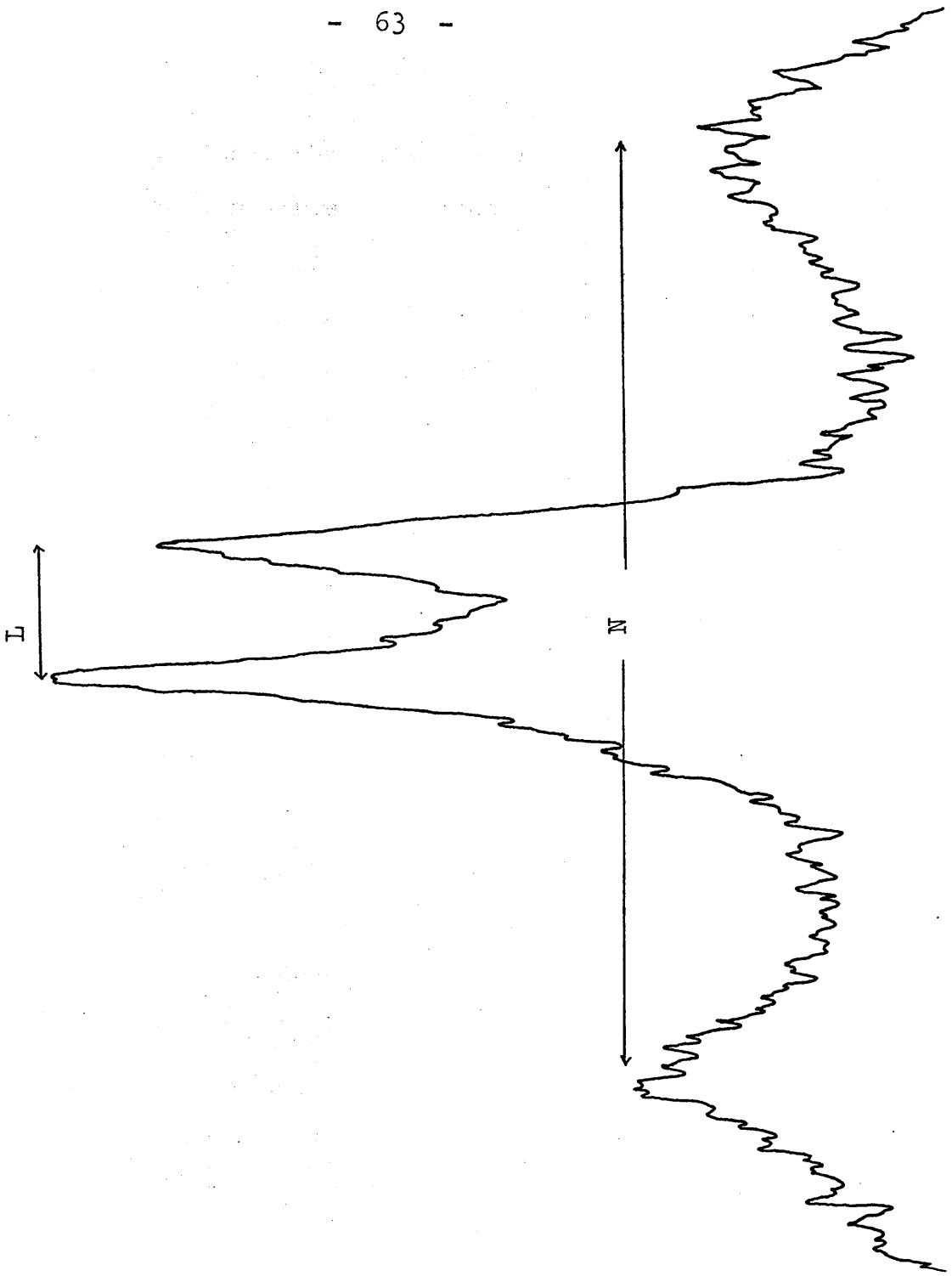
II. Metal-methyl complexes.

The ^1H n.m.r. spectra of complexes of the form

trans-$(R_3P)_2MMeCl$ (M = Pd,Pt) show a 1:2:1 triplet for the methyl resonance due to coupling to the two equivalent phosphorus atoms. In the platinum compounds, coupling of the methyl group to ^{195}Pt leads to formation of satellite triplets on each side of the main resonance. The compounds cis-$(R_3P)_2PtMeCl$ have a methyl resonance split into four lines of equal intensity by the non-equivalent phosphorus atoms, and these are split into 1:4:1 triplets by ^{195}Pt.

The fact that these complexes exhibit such characteristic spectra aids the study of the reactions between cis-$(R_3P)_2PtCl_2$ (R_3 = Et_3, Bu_3, Me_2Ph) and Me_2Hg. In all these reactions the resonance associated with the methyl group bonded to platinum can be detected after 5 or 6 days. Equilibrium is generally reached after 25 to 30 days, some Me_2Hg remaining (τ (Me)9.75 in $CDCl_3$) MeHgCl is produced in the reactions and characterised by a peak at 8.9 τ in $CDCl_3$. Satellite peaks due to coupling of the methyl protons to ^{199}Hg (I = $\frac{1}{2}$ abundance 17%), are also observed $J(^{199}Hg\text{-}H)$ = 204Hz[56]. These satellites make identification of methylmercury compounds unique. Initial formation of cis-$(R_3P)_2PtMeCl$ was not noted in any of the reactions.

The spectrum from the methyl groups in cis-$(R_3P)_2PtMe_2$ complexes is of the $X_3AA^1X_3^1$ type, split further by interaction with platinum. As an example, cis-$(Me_2PhP)_2PtMe_2$ exhibits a set of peaks centred at 9.40τ in $CDCl_3$. Satellite peaks are also observed, $J(^{195}Pt\text{-}H)$67Hz. The set of peaks at 9.40τ was expanded and the spectrum shown in figure 6. As described earlier, a doublet of separation $N = |J_{AX} + J_{AX^1}|$ forms part of the X resonance of an $XnAA^1Xn^1$ spectrum, and in this case N = 2Hz. The low value of N suggests that the two couplings J_{AX} and J_{AX^1} are of opposite sign. This is confirmed by the fact that the 'inner' lines are observed outside the central doublet, i.e. L ($= |J_{AX} - J_{AX^1}|$), the separation between the two sets of 'inner' lines is greater than N. The 'inner' lines are not well resolved but L is approximately 14Hz, with the result that $^3J(PPtCH)$ is $\pm$8Hz and $^3J(P^1PtCH)$ is $\mp$6Hz. It should be noted that it is not possible to deduce whether a certain $^3J(PPtCH)$ refers to the phosphorus trans or cis to the methyl group. The methyl region of the spectrum of $(Me_2PC_2H_4PMe_2)PtMe_2$ was also examined in detail yielding a value for L of 15.5Hz, and for N of 0.8Hz. Values of



Methyl region of cis-$(Me_2PhP)_2PtMe_2$ centred at τ 9.40

FIGURE 6.

^3J(PPtCH) are, therefore, $\pm$8.15Hz and $\mp$7.35Hz. The parameters observed for these two complexes agree closely with those determined for cis-$(Et_3P)_2PtMe_2$ by Allen and Pidcock[57]. Table 3 lists the n.m.r. parameters for the monomethyl and dimethyl derivatives studied.

The dimethyl palladium complex exhibits interesting n.m.r. spectra in different solvents. Thus, immediately $(Et_3P)_2PdMe_2$ is dissolved in $CDCl_3$ the solution turns yellow and a gas is evolved. The spectrum of the solution shows a 1:2:1 triplet centred at 9.8τ , J (P-H)6Hz, indicative of the formation of trans-$(Et_3P)_2PdMeCl$. The trans configuration is also demonstrated by the 1:4:6:4:1 pattern centred at 8.89τ observed for the methyl protons of the ethyl groups. Weak acids are known to react with $(Et_3P)_2PdMe_2$, and the first step in the reaction with ethanol is thought to involve the formation of the ethoxide $(Et_3P)_2Pd(OEt)Me$ with the elimination of methane[22]. Deuterochloroform would also appear to act as a weak acid forming trans-$(Et_3P)_2PdMeCl$ and liberating a gas, possibly CDH_3 plus C_2Cl_4. No reaction occurs when $(Et_3P)_2PdMe_2$ is dissolved in C_6D_6 and two distinct methyl resonances are detected in the n.m.r. spectrum. A triplet centred at 10.10τ , J(P-H)6Hz, is assigned to the trans-$(Et_3P)_2PdMe_2$ complex. A set of resonances, with an intensity a third

TABLE 3.

N.m.r. data for metal-methyl complexes.

COMPLEX	SOLVENT	τ (Me)	J(P-H)Hz	J(Pt-H)Hz	J(PPtCH + P^1PtCH)Hz
trans-$(Et_3P)_2PdMeCl$	$CDCl_3$	9.80	6		
	C_6D_6	9.62	6		
trans-$(Et_3P)_2PtMeCl$	$CDCl_3$	9.67	6	85	
trans-$(Bu_3P)_2PtMeCl$	$CDCl_3$	9.70	6	86	
trans-$(Me_2PhP)_2PtMeCl$	$CDCl_3$	9.83	6	84	
cis-$(Me_2PhP)_2PtMeCl$	$CDCl_3$	9.22	5 5		
cis-$(Ph_3P)_2PtMeCl$	$CDCl_3$	9.28	5 5		
trans-$(Et_3P)_2PdMe_2$	C_6D_6	10.10	6		
cis-$(Et_3P)_2PdMe_2$	C_6D_6	9.55			<2
cis-$(Me_2PhP)_2PtMe_2$	$CDCl_3$	9.40			2
cis-$(Ph_3P)_2PtMe_2$	$CDCl_3$	9.56			2
$(Me_2PC_2H_4PMe_2)PtMe_2$	C_6D_6	8.97			1

that of the triplet, centred at 9.55τ is assigned to the cis isomer of $(Et_3P)_2PdMe_2$. The value of N for cis-$(Et_3P)_2PdMe_2$ is less than 2Hz.

When one equivalent of $HgCl_2$ is added to a solution of $(Et_3P)_2PdMe_2$ in C_6D_6 the peaks centred at 10.10τ and 9.55τ are replaced by a triplet at 9.62τ , J(P-H)6Hz corresponding to the formation of trans-$(Et_3P)_2PdMeCl$. Dimethylmercury (9.84τ) and MeHgCl(8.9τ) are also detected.

Mercuric halides also react readily with dimethyl platinum complexes, and n.m.r. studies of these reactions enable the stereochemistry of the initial reaction product to be determined. Thus, immediate examination of the reaction between $HgCl_2$ and cis-$(Me_2PhP)_2PtMe_2$ in $CDCl_3$ shows the presence of the monomethyl compound cis-$(Me_2PhP)_2PtMeCl$, 9.22τ , Me_2Hg and MeHgCl. In the cis-monomethyl complex the methyl groups bonded to one phosphorus are no longer equivalent to those bonded to the other and the central doublets associated with each type can be detected. The satellite doublets due to coupling with ^{195}Pt are also visible for the methyls on the phosphorus trans to chloride. Although cis-$(Me_2PhP)_2PtMeCl$ is the initial product of the

$HgCl_2$/cis-$(Me_2PhP)_2PtMe_2$ reaction, cis-trans isomerism occurs and after two days no cis complex remains. Similar results are observed in the $HgCl_2$/cis-$(Ph_3P)_2PtMe_2$ reaction.

$$\text{cis-}(R_3P)_2PtMe_2 + HgCl_2 \xrightarrow{\text{fast}} \text{cis-}(R_3P)_2PtMeCl + MeHgCl + Me_2Hg$$

$$\text{cis-}(R_3P)_2PtMeCl \xrightarrow{\text{slow}} \text{trans-}(R_3P)_2PtMeCl$$

The rate of isomerisation is greatly increased with size of halogen, since the HgI_2/cis-$(Me_2PhP)_2PtMe_2$ reaction mixture produces approximately four times as much trans-$(Me_2PhP)_2PtMeI$ (9.67 τ) as cis- (9.15 τ) within 20 minutes. The dimethyl complexes containing the chelating phosphines $Me_2PC_2H_4PMe_2$ or $Ph_2PCH_2PPh_2$ also react rapidly with $HgCl_2$. In these cases, however, the compounds produced are too insoluble for detailed study. Peaks due to Me_2Hg and MeHgCl can be observed, however. The spectrum of the insertion compound $(PPh_3)_2Pt_2(COMe)_2Cl_2$ was recorded in $CDCl_3$. The methyl resonance is centred at 8.74 τ and is split into a doublet by coupling to one phosphorus, J(P-H)8Hz. Further coupling to ^{195}Pt occurs, J(PtH)57Hz, giving the pattern of a 1:4:1 triplet of doublets. It is interesting to note that the methyl resonance of the acetyl group in the platinum IV complexes

$(Me_2PhP)_2PtMe_2X(COMe)$ (X = Cl,Br) consists only of a 1:4:1 triplet, J(PtH)58Hz, no coupling to phosphorus being observed[51].

Finally, the n.m.r. parameters for the methyl groups directly bonded to platinum and for the groups of the Me_2PhP ligand are listed in table 4 for the complexes prepared with this phosphine. The values are substantiated in recent work by Ruddick and Shaw[51]. The platinum-methyl coupling constants $^3J(PtH)$, for the methyl groups bonded to phosphorus, are found to decrease in the order of trans-ligand halogen > P > C. The behaviour of $^3J(PtH)$ is paralleled by that of $^2J(PtH)$ for the methyls directly bonded to the metal. A semiempirical equation has been used successfully for $^2J(XCH)$ in which the coupling is assumed to be directly proportional to the σ-character of the hybrid X orbital used in the X-C bond[16]. The strength of the platinum-carbon bond also depends on the nature of the trans-ligand and decreases in the order of trans-ligands halogen > P > C. The amount of platinum σ-orbital character in the platinum-methyl bond probably decreases in the same order and hence this can explain the order of decreasing $^2J(PtH)$.

TABLE 4

N.m.r. data for Me_2PhP complexes of platinum.

COMPLEX	Me groups (phosphorus)									Me groups (platinum)					
	trans ligand									trans ligand					
	halogen			P			C			halogen			P		
	τ	J(PH)	J(PtH)	τ	J(PH)	J(PtH)	τ	J(PH)	J(PtH)	τ	J(PH)	J(PtH)	τ	J(PH)	J(PtH)
cis-L_2PtCl_2	8.23	11	35												
cis-$L_2PtMeCl$	8.47	10	44				8.37	8					9.22	5 5	
cis-L_2PtMeI	8.05	4	47										9.15		
cis-L_2PtMe_2							8.51	8	20				9.40		67
trans-$L_2PtMeCl$				8.15	7	29				9.86	6	84			
trans-L_2PtMeI				8.02	7	29				9.67	7	81			
trans-$L_2PtPhCl$				8.51	7	32									

L = Me_2PhP

(b) Infra-red

The vibrational spectra of palladium II and platinum II complexes with phosphines have been extensively examined[58]. Assignments for the characteristic frequencies of the complexes prepared in this work are listed in tables 5 and 6. The compounds cis-$(R_3P)_2PtCl_2$ are regarded as having C_{2v} symmetry and the two Pt-Cl stretching frequencies predicted on this basis are detected in the region of 300 cm^{-1}. Two Pt-P stretches are observed at about 430 cm^{-1} in several of the complexes, but in others the peaks are obscured by other ligand vibrations. Species of the type cis-$(R_3P)_2PtMe_2$ exhibit two Pt-C stretching frequencies in the 500-540 cm^{-1} range, the corresponding symmetrical deformation frequencies, $\delta_s(Me)$, being observed in the 1170-1210 cm^{-1} region[31]. The square-planar complexes trans-$(R_3P)_2MXY$ (M = Ni, Pd, Pt; X = Cl; Y = Cl, Me, Ph, o-tolyl) show only one metal-chlorine stretch, and thus distinction between the cis- and trans- dichlorides can be made by infra-red. Although both symmetric and asymmetric M-P stretching vibrations are infra-red active, in the latter complexes only the asymmetric vibration is observed, the symmetric stretching band being too weak to be detected[59].

TABLE 5

I.r. parameters for metal dihalide complexes

COMPLEX	ν (M-Cl) cm^{-1}		ν (M-P) cm^{-1}	
	ν (M-Cl) sym.	ν (M-Cl) asym.	ν (M-P) sym.	ν (M-P) asym.
cis-$(Et_3P)_2PtCl_2$	300m	275s	439m	422m
cis-$(Bu^n_3P)PtCl_2$	300s	275s	452s	403m
cis-$(Me_2PhP)_2PtCl_2$	306m	285m	452m	433w
cis-$(Ph_3P)_2PtCl_2$	315m	293m		
$(Me_2PC_2H_4PMe_2)PtCl_2$	308s	300sh	462m	
$(Ph_2PCH_2)PtCl_2$	305m	284m		
$(EtSC_2H_4SEt)PtCl_2$	321s	312s		
trans-$(Et_3P)_2PdCl_2$	355m		410w	

All spectra were recorded as KBr discs

m = medium; s = strong; sh = shoulder; w = weak

TABLE 6

I.r. parameters for organometallic complexes

COMPLEX	ν (M-Cl) cm^{-1}	ν (M-P) cm^{-1}	ν (M-C) cm^{-1}	δ (Me(s)) cm^{-1}
trans-$(Et_3P)_2PtPhCl$	280m	410m	492v.w.	
trans-$(Me_2PhP)_2PtPhCl$	274m	419m		
$(EtSC_2H_4SEt)PtPhCl$	309m			
trans-$(Bu^n_3P)_2PtMeCl$	272m	390m	550w	1220m
cis-$(Et_3P)_2PtMe_2$		415m,br	524m,508s	1200w,1179m
cis-$(Me_2PhP)_2PtMe_2$		433m,420m	532m,519s	1198w,1172m
cis-$(Ph_3P)_2PtMe_2$			532m	1212w,1192m
$(Me_2PC_2H_4PMe_2)PtMe_2$		445m	515sh,510s	1190w,1170v.w.
$(Ph_2PCH_2PPh_2)PtMe_2$				1210sh,1185m
trans-$(Et_3P)_2PdPhCl$	299m	408m		
trans-$(Ph_3P)_2Ni$(o-tolyl)Cl	334m			

All spectra were recorded as KBr discs

The metal-chlorine stretching vibration in the compounds is very sensitive to the nature of the metal and the trans ligand. In the complexes trans-$(R_3P)_2MCl_2$ (M = Ni, Pd, Pt) it has been shown[60] that ν(M-Cl) is in the 403-408 cm^{-1} region for Ni, 353-359 cm^{-1} for Pd and 326-339 cm^{-1} for Pt. The effect of altering the trans-ligand also results in a marked shift in the position of the vibration. Thus, we observe the metal-halogen stretch in trans-$(Ph_3P)_2Ni$(o-tolyl)Cl at 334 cm^{-1}, in trans-$(Et_3P)_2PdPhCl$ at 299 cm^{-1} and in trans-$(Et_3P)_2PtPhCl$ at 280 cm^{-1}. To generalise on the values of ν(M-Cl) for the complexes prepared in this work, ν(M-Cl) decreases in the order of trans-ligand $Cl > PR_3 >$ alkyl or aryl, i.e. the trans-influence (as defined in reference 24) of chloride $<$ 'phosphine' $<$ alkyl or aryl. These effects have been discussed previously[61].

Some infra-red parameters for the carbonyl complexes cis-$(PR_3)(CO)PtCl_2$ (R = Bu, Ph) and the products of their reactions with Ph_2Hg, Me_2Hg, PhMgBr and MeLi are listed in table 7. The starting materials show a terminal C-O stretch in the 2100 cm^{-1} region. The values of ν(CO) for the products of these complexes with organomercurials are in the 1620-1665 cm^{-1} region, indicating carbonyl

TABLE 7

I.r. parameters for metal carbonyl complexes

COMPLEX	ν(CO)cm^{-1}	ν(M-Cl)cm^{-1}	ν(M-O)cm^{-1}	δ(MCO)cm^{-1}
cis-$(Ph_3P)(CO)PtCl_2$	2100s	310s,305m		
cis-$(Bu_3P)(CO)PtCl_2$	2095v.s.	298sh,295m		
$(Bu_3P)(CO)PtMe_2$ [a]	2030s			
$(Bu_3P)(CO)PtPh_2$ [a]	2060s			
$(Ph_3P)_2Pt_2(COPh)_2Cl_2$	1645s	269m		650m
$(Bu_3P)_2Pt_2(COPh)_2Cl_2$	1625v.s.	280sh,269m	475sh	654s
$(Et_3P)_2Pt_2(COPh)_2Cl_2$	1620v.s.	290sh,270m	480w	657s
$(Bu_3P)_2Pt_2(COPh)_2Br_2$	1626m		488w	660m
$(Ph_3P)_2Pt_2(COMe)_2Cl_2$	1665s	289w,269m		592m
$(Bu_3P)_2Pt_2(COMe)_2Cl_2$ [a]	1650s		535m	595m
trans-$(Ph_3P)_2(CO)IrCl$	1955s	315m		
$(Ph_3P)_2(CO)ClIr(HgPh)Ph$	2000s	304w		

(a) recorded as films, others recorded as KBr discs

insertion, the acetyl complexes showing slightly higher values than their benzoyl analogues. The carbon-oxygen stretching frequencies are lower than those in organic saturated open-chain ketones but resemble those found for the mononuclear derivatives trans-$(Et_3P)_2M(COMe)X$[62]. Adams and Booth[62] found two bands in the 500-600 cm^{-1} range for their acetyl complexes, and assigned a skeletal deformation to the higher band (ca. 580 cm^{-1}). The lower band, and also the weaker, was taken to be the metal-carbon stretch. Using their assignments the complexes $(R_3P)_2Pt_2(COMe)_2Cl_2$ show deformation modes at 595 cm^{-1} for R = Bu and 592 cm^{-1} for R = Ph. A medium intensity band at 535 cm^{-1} in the tributylphosphine complex is attributed to the platinum-carbon stretch. This band is obscured in the triphenylphosphine analogue. The skeletal deformation mode δ (Pt-C-O) of the benzoyl complexes is found at higher frequencies (ca. 650 cm^{-1}) and the platinum-carbon stretch at lower frequencies (ca. 480 cm^{-1}) than in the acetyl derivatives. Confirmation of the assignment of the band at 650 cm^{-1} in $(Ph_3P)_2Pt_2(COPh)_2Cl_2$ to the δ (Pt-C-O) mode was obtained by examining the spectrum of its decarbonylated product, $(Ph_3P)_2Pt_2Ph_2Cl_2$, which shows no peaks at 1645 cm^{-1} [ν (CO)] or 650 cm^{-1} [δ (PtCO)].

Symmetrical trans chloride-bridged compounds $(R_3P)_2Pt_2Cl_4$ show two bands associated primarily with stretching of platinum-chlorine bonds in the bridge. The stretching frequencies of the Pt-Cl bonds trans to R_3P have been shown[63] to be in the region of 260 cm^{-1}. All the chloro-bridged complexes prepared in this work show a peak at approximately 270 cm^{-1} and this is assigned to the stretching of the platinum-chlorine bond trans to the phosphine. In certain cases a shoulder is observed on the high frequency side of this peak, being well resolved at 289 cm^{-1} for $(Ph_3P)_2Pt_2(COMe)_2Cl_2$. This is tentatively attributed to the Pt-Cl stretch of the bond trans to -COR.

Values of ν(CO) for trans-$(Ph_3P)_2$(CO)IrCl and its product with Ph_2Hg are also given in table 7. The stereochemistry of the Ir III complex $(Ph_3P)_2$(CO)ClIr(HgPh)Ph cannot be determined. However, the position of the Ir-Cl stretching vibration at 304 cm^{-1} indicates that the chloride ligand remains trans to CO, similar values of ν(Ir-Cl) having been recorded[64] for Ir III complexes for which it is known that CO is trans to chloride.

The reaction between cis-(Bu_3P)(CO)$PtCl_2$ and excess PhMgBr produces both the insertion complex

$(Bu_3P)_2Pt_2(COPh)_2Br_2$ [ν(CO) 1626 cm^{-1}] and the disubstituted derivative $(Bu_3P)(CO)PtPh_2$ [ν(CO) 2060 cm^{-1}] . The spectrum of the latter compound also exhibits a medium peak at 1745 cm^{-1} and this is thought to arise from the oxidation of the diphenyl carbonyl species to the carbonate. A known platinum-carbonate complex, $(Ph_3P)_2PtCO_3$, shows a peak at 1680 cm^{-1} [65].

Finally, table 8 lists some of the most characteristic features of the i.r. spectra of the organomercurials, both starting materials and by-products, which we have examined. Only the lowest frequency X-sensitive stretching vibration (t), ν(Hg-C), is listed for the aryl compounds.[66]

TABLE 8

I.r. data for organomercurials

COMPLEX	ν(Hg-C)cm^{-1}	ν(Hg-Cl)cm^{-1}	δ(Me)cm^{-1}
$(C_6H_5)_2Hg$	250m		
$(o\text{-}CH_3C_6H_4)_2Hg$	257m		
$(C_6H_5)HgCl$	232m	325m	
$(o\text{-}CH_3C_6H_4)HgCl$	238m	318m	
MeHgCl	538m	299m	785s,br
MeHgI	520m		760s,br

Recorded as KBr discs

5. EXPERIMENTAL

All reactions involving air-sensitive intermediates were performed under an atmosphere of nitrogen. Organomercurials were handled with extreme caution in a well-ventilated fume hood and apparatus contaminated with these reagents was washed with a CCl_4/Br_2 solution. Infra-red spectra were recorded on a P.E.225 spectrometer, melting points on a Kofler hot-stage microscope, and ^1H n.m.r. spectra were measured at 33° on a P.E. R.10 instrument at 60M.Hz. Organomercuric by-products from the reactions were identified by comparing melting points and infra-red spectra with those of authentic samples.

Typical methods of preparation of starting materials are described first in this section followed by the description of the reaction of these complexes with mercurials.

Preparation of ligands

Dimethylphenylphosphine[67]

A solution of $PhCl_2P$ (76ml, 0.56mol.) in dry ether (100ml.) was added dropwise to an ethereal solution (400ml.) of MeMgI [prepared from Mg(40g, 1.67mol.) and MeI(102ml., 1.65mol.)]. The solution was refluxed for 2 hours. After cooling to 0°, the mixture was treated

with an excess of a saturated NH_4Cl solution. The ethereal layer was separated and washed with water, then it was dried over Na_2SO_4. A fractional distillation at atmospheric pressure, under nitrogen, gave the colourless liquid dimethylphenylphosphine (22g., 30%) b.p. 185°/755 m.m.Hg.

P,P,P^1,P^1 - Tetramethylethylenediphosphine[68]

The reaction steps are shown below:-

$$SPCl_3 + 2MeMgBr \longrightarrow Me_2P(S)-P(S)Me_2$$

$$Me_2P(S)-P(S)Me_2 + C_2H_4 \longrightarrow Me_2P(S)C_2H_4P(S)Me_2$$

$$Me_2P(S)C_2H_4P(S)Me_2 + 2Bu_3P \longrightarrow Me_2PC_2H_4PMe_2 + 2Bu_3PS$$

In the first stage, tetramethylbiphosphinedisulphide [(95g., 85%) m.p.226-227°] was prepared from $SPCl_3$(208g., 1.5mol.) and MeMgBr(4mol.) in ether (1500ml.) Ethylene (ca. 3g., 0.1mol.) was then condensed into a Carius tube (ca. 165ml.) containing $Me_2P(S)P(S)Me_2$ (15.2g., 0.085mol.) and KI (0.3g.) The tube was heated at 275° for 48 hours and the light yellow crystalline product was recrystallised from ethanol to give off-white needles of P,P,P^1,P^1 - tetramethylethylenediphosphine-disulphide (11.4g., 50%) m.p. 265-267°.

A mixture of $Me_2P(S)C_2H_4P(S)Me_2$ (11.4g., 0.05mol.) and Bu_3P (26ml., 0.1mol.) was heated to 240° in a 100ml.

flask fitted to a distillation apparatus. The mixture soon became homogeneous and a colourless liquid distilled over at 160-190° during a period of 1 hour. Redistillation gave P,P,P^1,P^1 - tetramethylethylenediphosphine (5g., 66%).

Preparation of Platinum complexes.

cis-bisdimethylphenylphosphineplatinumIIchloride

K_2PtCl_4(8.3g., 20m.mol.) was suspended in ethanol (150ml.) and Me_2PhP(5.2g., 38m.mole) was added. The solution was refluxed for 24 hours, solvent was removed, and the residue was washed with water (ca. 100ml.) The off-white material was recrystallised from ethanol to give white crystals of cis-bisdimethylphenylphosphineplatinum II chloride (5.4g., 50%) m.p. 198-200°.

The melting points of the other platinum complexes prepared by a similar procedure are shown below. All the compounds are white crystalline solids.

COMPLEX	M.Pt(°C)
cis-$(Et_3P)_2PtCl_2$	192-193
cis-$(Bu_3P)_2PtCl_2$	144-145
cis-$(Ph_3P)_2PtCl_2$	307-310 (dec)
$Ph_2PCH_2PPh_2PtCl_2$	ca. 330

cis-bisdimethylphenylphosphinedimethylplatinum[5]

cis-$(Me_2PhP)_2PtCl_2$(1.4g., 2.6m.mol.) was suspended in

dry benzene (30ml.) and MeLi(5ml., 1.95m) was added. The solution was stirred at ca.50° for 2½ hours, and after cooling to room temperature, water (20ml.) was added and the layers were separated. The organic layer was dried over $MgSO_4$. The light yellow residue, obtained on removal of the solvent, was recrystallised from light petroleum (b.p. 40-60°) to give off-white crystals of cis-bisdimethylphenylphosphinedimethylplatinum (0.85g., 65%) m.p. 73-75°. The melting points of the other dimethyl derivatives are shown.

COMPLEX	M.Pt.(°C)
cis-$(Et_3P)_2PtMe_2$	81-82
cis-$(Ph_3P)_2PtMe_2$	234-236 (dec)
$Me_2PC_2H_4PMe_2PtMe_2$	143-145 (dec)

Dichloro-di-μ-chlorobistributylphosphinediplatinum[69]

cis-$(Bu_3P)_2PtCl_2$ (6.1g., 9m.mol.) was dissolved in sym-tetrachloroethane (225ml.) $PtCl_2$ (2.9g., 11m.mol.) was added and the solution was refluxed for 1½ hours. On cooling, the mixture was filtered and solvent was removed on the rotary evaporator. The residue was recrystallised from chloroform to yield orange crystals of dichloro-di-μ-chlorobistributylphosphinediplatinum (6g., 70%) m.p. 143-144°. The other chloro-bridged

binuclear complexes $(Ph_3P)_2Pt_2Cl_4$ [m.p. 270-280°(dec)] and $(Et_3P)_2Pt_2Cl_4$ (m.p. 223-224°) were also prepared by this method. Treatment of $(Et_3P)_2Pt_2Cl_4$ with KBr in acetone (2 hours at R.T.) led to metathetical replacement of chloride by bromide with formation of $(Et_3P)_2Pt_2Br_4$ (m.p. 205-206°).

cis-tributylphosphinecarbonylplatinum II chloride[69]

$(Bu_3P)_2Pt_2Cl_4$ (6g., 6.5m.mol.) was dissolved in benzene (150 ml.) and carbon monoxide was bubbled through the solution for 12 hours. The solvent was removed under reduced pressure and the residue recrystallised from ethanol to give colourless crystals of cis-tributylphosphinecarbonylplatinum II chloride (3.5g., 55%) m.p. 115-116°.

Crystals of the analogous triphenylphosphine complex cis-$(Ph_3P)(CO)PtCl_2$ were prepared similarly (40%, m.p. 220-230°).

Preparation of organomercurials.

Di(o-tolyl) mercury.

Mercuric chloride (10g., 38m.mole) was added to (o-tolyl)MgBr [from Mg(2.4g., 100m.mol.) and o-bromobenzene (17g., 100m. mole) in benzene (100 ml.) and ether (70 ml.)], and the solution was refluxed for 5 hours. After this

period, the flask was cooled in an ice-bath and the excess Grignard reagent hydrolysed by water. Chloroform (ca. 200 ml.) was then added and the layers were separated, the organic layer being dried over $MgSO_4$. Solvent was removed under vacuum and the residue was recrystallised from chloroform to yield colourless crystals of o-tolylmercuric bromide (3.5g., 25%) m.p. 169-170°. (o-tolyl)HgBr (3.5g., 9.5m. mol.) was dissolved in hot acetone (60 ml.) and a solution of PPh_3(2.4g., 9.5m.mol.) in acetone (20 ml.) was added[70]. Formation of crystals of $(Ph_3P)_2HgBr_2$ occurred almost immediately and after 30 minutes this precipitate was filtered off and was dried (3.87g., 90%) m.p. 261-270° (dec). The filtrate was taken to dryness and the residue extracted with ether (50 ml.) The ether was reduced to small volume causing precipitation of white crystals of <u>di(o-tolyl)mercury</u> (1.26g., 70%) m.p. 105-107°.

Me_2Hg(b.p. 92°, 750m.m./Hg) and Ph_2Hg(m.p.124-125°) were prepared by the action on $HgCl_2$ of MeMgI and PhMgBr respectively[37]. The yields were 75% and 60%.

<u>Reactions between the metal complexes and diaryl mercurials.</u>

<u>cis-bisdimethylphenylphosphineplatinum II chloride and diphenylmercury</u>.

To a solution of cis-$(Me_2PhP)_2PtCl_2$ (0.5g.,0.9m.mol.)

in ethanol (40 ml.) was added Ph_2Hg (0.33g., 0.9m.mol.) The mixture was heated under reflux overnight, after which solvent was removed under reduced pressure. The residue was heated in a sublimation apparatus (70°/1m.m.Hg) and PhHgCl (0.27g., 90%) was sublimed off to leave a white crystalline residue of

trans-bisdimethylphenylphosphinephenylplatinum chloride

(0.31g., 55%) m.p. 119-120° (from ethanol). (Found: C, 45.0; H, 4.55%. $C_{22}H_{27}ClP_2Pt$ requires C, 45.25; H, 4.65%).

1,2-bisdiphenylphosphinomethaneplatinum II chloride and diphenyl mercury

$(Ph_2PCH_2PPh_2)PtCl_2$ (0.32g., 0.5m.mol.) was suspended in ethanol (40 ml.) and Ph_2Hg (0.18g., 0.5m.mol.) was added. The mixture was refluxed overnight, the milky solution being replaced by a light yellow solution. On cooling, the solvent was distilled off and PhHgCl (0.12g., 75%) sublimed from the residue, which was then recrystallised from ethanol giving light-yellow plates of

1,2-bisdiphenylphosphinomethanephenylplatinum II chloride

(0.11g., 30%).

1,2-Bisethylthioethaneplatinum II chloride and diphenylmercury.

Diphenylmercury (0.36g., 1m.mol.) was added to a

suspension of $(EtSC_2H_4SEt)PtCl_2$ (0.42g., 1m.mol.) in ethanol (40 ml.) The suspension was heated under reflux for 12 hours to give a light yellow solution, some metal being deposited. Solvent was removed and PhHgCl(0.22g., 70%) was sublimed off from the residue (90°/1m.m.Hg). The residue was recrystallised twice from ethanol to give pale yellow needles of 1,2-bisethylthioethanephenylplatinum chloride (0.23g.,50%) m.p. 157-158° (Found: C, 31.5; H, 4.15%. $C_{12}H_{19}ClPtS_2$ requires C, 31.45; H, 4.2%.)

Dichloro-di-μ-chlorobistriethylphosphinediplatinum and diphenylmercury

Diphenyl mercury (0.7g., 2m.mol.) was dissolved in benzene (70 ml.) and $(Et_3P)_2Pt_2Cl_4$ (0.76g., 1m.mol.) was added. The suspension was stirred at room temperature for 18 hours, and after this time, the solution, which had become very dark, was filtered. Solvent was removed and the residue was sublimed at 100°/0.05m.m.Hg to give PhHgCl(0.22g.,30%). The brown material which remained was recrystallised twice from acetone yielding white crystals of trans-bistriethylphosphinediphenylplatinum (0.24g., 20%) m.p. 175-176° (lit. 176-180°).

Dibromo-di-μ-bromobistriethylphosphinediplatinum and di(o-tolyl) mercury.

$(Et_3P)_2Pt_2Br_4$(0.63g., 0.66m.mol.) was suspended in benzene

(15 ml.) and di(o-tolyl) mercury (0.50g., 1.34m.mol.) was added. The solution immediately darkened and was stirred at room temperature for 18 hours. After this time, the solution was filtered and solvent was removed under reduced pressure leaving a brown solid. This material was fractionally recrystallised from acetone giving cream crystals of di(o-tolyl)-di-μ-bromo-bistriethylphosphinediplatinum (.11g., 10%).

trans-bistriethylphosphinepalladium II chloride and diphenylmercury

Diphenylmercury (0.35g., 1m.mol.) was added to a solution of trans-$(Et_3P)_2PdCl_2$ (0.42g., 1m.mol.) in ethanol (40ml.) and the mixture was heated under reflux for 2 hours. A small deposit of metal was filtered off and the solution was cooled, causing PhHgCl (0.22g., 70%) to crystallise out. Solvent was distilled off under reduced pressure and the residue was crystallised from ethanol and then hexane to give plates of trans-bistriethylphosphinephenyl-palladium II chloride (0.22g., 45%) m.p. 101-102° (Found: C, 45.2; H, 7.8%. $C_{18}H_{35}ClP_2Pd$ requires C, 45.35; H, 7.75%).

Bistriphenylphosphinenickel II chloride and di-o-tolyl-mercury

Di-o-tolyl-mercury (0.39g., 1m.mol.) was added to a suspension of $(Ph_3P)_2NiCl_2$ (0.64g., 1m.mol.) in benzene

(50 ml.) and the mixture was heated under reflux for 2 hours. The mixture turned orange and some decomposition was evident. On cooling to 0°, a precipitate was produced which contained green $(Ph_3P)_2NiCl_2$ (0.1g.), white $(o\text{-tolyl})_2Hg$, Ph_3P and (o-tolyl)HgCl (i.r. identification). The solvent was reduced in volume and a yellow powder was deposited. This was recrystallised from ethanol to give yellow-orange crystals of bistriphenylphosphine-o-tolyl-nickel II chloride m.p. 153-156°(dec). (Found: C, 71.5; H, 5.8%. $C_{43}H_{37}ClNiP_2$ requires C, 72.8; H, 5.25%). The mass spectrum failed to show a molecular ion, but fragments with masses corresponding to Ph_3P and (o-tolyl)NiCl were observed.

Reactions between the metal complexes and dimethylmercury

cis-bistri-n-butylphosphineplatinum II chloride and dimethylmercury

A solution of cis-$(Bu_3P)_2PtCl_2$ (0.28g., 0.4 m.mol.) in dimethylmercury (10g.) was heated under reflux for 3 hours. Unchanged dimethylmercury was removed under vacuum and the yellow oil remaining was heated in a sublimation apparatus. Methylmercuric chloride (70mg., 70%) sublimed off to leave a yellow waxy residue which contained a little mercury. Recrystallisation of

the residue from light petroleum (b.p. 40-60°) containing active charcoal gave pale yellow plates of trans-bistri-n-butylphosphinemethylplatinum II chloride (0.1g., 37%) m.p. 39-40° (Found: C, 45.8; H, 8.75%. $C_{25}H_{57}ClP_2Pt$ requires C, 46.05; H, 8.85%).

In a separate experiment, cis-$(Bu_3P)_2PtCl_2$ (0.31g., 0.66m.mol.) and Me_2Hg(0.15g., 0.67m.mol.) were dissolved in $CDCl_3$ (ca. 1ml.) and the progress of the reaction was followed by n.m.r. spectroscopy at 33°. The appearance and growth of the triplet centred at 9.70τ, associated with the methyl resonance of trans-$(Bu_3P)_2PtMeCl$, allowed the progress of the reaction to be studied. Equilibrium was reached after 18 days; some starting materials remained unchanged.

cis-bisdimethylphenylphosphineplatinum II chloride and dimethylmercury

A solution of cis-$(Me_2PhP)_2PtCl_2$ (0.092g., 0.17m.mol.) and Me_2Hg (0.09g., 0.38m.mol.) in $CDCl_3$ (ca. 1ml.) was placed in an n.m.r. tube with 2 drops of T.M.S. as internal standard. The development of the triplet centred at τ 9.83 (and satellite triplets) caused by the methyl-Pt group of trans-$(Me_2PhP)_2PtMeCl$ was observed; equilibrium was reached after 17 days at 33°. The final

spectrum confirmed the presence of trans-$(Me_2PhP)_2PtMeCl$ and MeHgCl, as well as unchanged starting materials.

$(Et_3P)_2MCl_2$ [M = Pd, Pt] and dimethylmercury

Reactions between the metal complexes and dimethylmercury were examined by n.m.r. spectrometry as above. With cis-$(Et_3P)_2PtCl_2$, equilibrium was reached after 16 days. No reaction was observed between the trans-complexes trans-$(Et_3P)_2MCl_2$ (M = Pd, Pt) and Me_2Hg after 30 days.

Reactions between organo-metallic complexes and mercuric salts

1,2-Bisethylthioethanediphenylplatinum and mercuric chloride

Mercuric chloride (0.27g., 1m.mol.) was added to a solution of $(EtSC_2H_4SEt)PtPh_2$ (0.5g., 1m.mol.) in tetrahydrofuran (50 ml.) and the mixture was heated under reflux for 6 hours. The solution was filtered to remove a slight deposit of metal, and solvent was removed under reduced pressure. Fractional crystallisation of the orange residue from ethanol gave phenyl-mercuric chloride (m.p. 251-252°) and 1,2-bisethylthioethanephenylplatinum II chloride m.p. 155-157°.

cis-Bistriethylphosphinediphenylplatinum and mercuric chloride

Mercuric chloride (0.27g., 1m.mol.) was added to a solution

of cis-$(Et_3P)_2PtPh_2$ (0.59g., 1m.mol.) in ethanol (40 ml.) and the mixture was heated under reflux for 4 hours. Solvent was removed under reduced pressure and the white residue was extracted with benzene (5 ml.) Phenylmercuric chloride (0.24g., 78%) remained undissolved. Solvent was removed from the filtrate which was recrystallised from ethanol to give trans-bistriethylphosphinephenylplatinum II chloride (0.38g., 69%) m.p. 106-107°. Its i.r. spectrum and m.p. were identical with those of an authentic sample.

cis-Bistriethylphosphinedimethylplatinum and mercuric iodide

Mercuric iodide (0.26g., 0.54m.mol.) was added to a solution of cis-$(Et_3P)_2PtMe_2$ (0.24g., 0.52m.mol.) in benzene (20 ml.) Reaction occurred over a period of 30 minutes to give a yellow solution. Solvent was removed under vacuum and methylmercuric iodide (0.09g., 55%) sublimed from the residue (80°/0.5m.m.Hg). The yellow-brown solid remaining was recrystallised from ethanol to give a mixture (as indicated by i.r.) of trans-bistriethylphosphinemethylplatinum II iodide. ν(Pt-C) 535cm^{-1} and trans-bistriethylphosphineplatinum II iodide.

cis-Bisdimethylphenylphosphinedimethylplatinum and mercuric chloride

Mercuric chloride (13.5 mg., 0.05m.mol.) and cis-$(Me_2PhP)_2PtMe_2$ (27mg., 0.05m.mol.) were mixed in $CDCl_3$ (1 ml.) in an n.m.r. tube. Immediate examination of the ^1H n.m.r. spectrum showed the presence of Me_2Hg(τ 9.75), MeHgCl(τ 8.90) and cis-$(Me_2PhP)_2PtMeCl$ (quartet centred at τ 9.22). After 12 days the quartet at τ 9.22 had completely disappeared and was replaced by triplets centred at τ 9.83 due to trans-$(Me_2PhP)_2PtMeCl$.

The reaction between cis-$(Me_2PhP)_2PtMe_2$ (133mg., 0.25m.mol.) and mercuric iodide (112mg., 0.25m.mol.) in $CDCl_3$ (1 ml.) within 20 minutes produced trans-$(Me_2PhP)_2PtMeI$ (τ 9.67) and cis-$(Me_2PhP)_2PtMeI$ (τ 9.15), the ratio of trans to cis being ca. 4 : 1. Methylmercuric iodide (τ 8.83) was also produced.

Similarly, reactions between mercuric chloride and cis-$(Ph_3P)_2PtMe_2$, $(Me_2PC_2H_4PMe_2)PtMe_2$ and $(Ph_2PCH_2PPh_2)PtMe_2$ were followed by ^1H n.m.r. spectroscopy. Resonances due to dimethylmercury and methylmercury chloride were instantly produced in each case.

Bistriethylphosphinedimethylpalladium and mercuric chloride

$(Et_3P)_2PdMe_2$ (0.37g., 1m.mol.) was added to a suspension of mercuric chloride (0.27g., 1m.mol.) in benzene (20 ml.)

The solution immediately turned yellow and was stirred for 18 hours at room temperature. Solvent was distilled off under reduced pressure and methylmercuric chloride (0.1g., 40%) was sublimed from the yellow residue (80°/0.5m.m.Hg). The yellow solid remaining, which was contaminated with metal, was recrystallised from ethanol to give yellow plates of trans-bistriethylphosphinepalladium II chloride (0.22g., 50%,) m.p. 140-141°. The i.r. spectrum was identical to that of an authentic sample.

In a separate experiment, equimolar amounts of $(Et_3P)_2PdMe_2$ and mercuric chloride were reacted in C_6D_6 (1 ml.) and the yellow solution immediately transferred to an n.m.r. tube. The spectrum showed the presence of trans-$(Et_3P)_2PdMeCl$ (τ 9.62) and dimethylmercury (τ 9.84).

Reaction between trans-$(Et_3P)_2PtPhCl$ and $Ph_2PC_2H_4PPh_2$

trans-$(Et_3P)_2PtPhCl$ (0.3g., 0.55m.mol.) was dissolved in benzene (40 ml.) and $Ph_2PC_2H_4PPh_2$ (0.22g., 0.55m.mol.) was added. The solution was set aside for 24 hours, during which time white crystals deposited. The solvent was filtered off under nitrogen and the crystals of 1,2-bisdiphenylphosphinoethanetriethylphosphinephenylplatinum chloride.benzene, $[(Ph_2PC_2H_4PPh_2)(Et_3P)PtPh]^+Cl^-C_6H_6$ were dried (0.33g., 75%) m.p. 222-223°.

(Found: C, 58.73; H, 5.66%. $C_{44}H_{50}ClP_3Pt$ requires C, 58.59; H, 5.56%).

Integration of the n.m.r. spectrum gave a ratio of aromatic to aliphatic protons of 31:19 which is correct for the above formulation. Addition of methyliodide to the filtrate from the reaction caused precipitation of white crystals of triethylmethylphosphonium iodide (0.11g., 80%).

Reactions between (phosphine)(carbonyl)platinum chlorides and organomercurials

cis-triphenylphosphinecarbonylplatinum II chloride and diphenylmercury

Diphenylmercury (0.35g., 1m.mol.) was added to a suspension of cis-$(Ph_3P)(CO)PtCl_2$ (0.56g., 1m.mol.) in benzene (40 ml.) The mixture turned yellow and was stirred at room temperature overnight. Solvent was removed and phenylmercuric chloride (0.2g., 65%) was sublimed from the residue (80°/0.5m.m.Hg). The light yellow solid remaining was dissolved in chloroform and hexane was added to the solution to give a pale yellow precipitate of di-μ-chloro-bistriphenylphosphinebisbenzoyl-diplatinum, $(Ph_3P)_2Pt_2(COPh)_2Cl_2$ (0.31g., 51%) m.p. 280° (dec) (Found: C, 49.3; H, 3.6%. $C_{50}H_{40}Cl_2O_2P_2Pt_2$ requires C, 50.2; H, 3.35%).

When heated for a prolonged period at 90°/1m.m.Hg the

i.r. band at 1645cm^{-1} associated with ν(CO), disappeared. Mass spectral data for this compound are listed in table 9.

cis-triphenylphosphinecarbonylplatinum II chloride and dimethylmercury

Dimethylmercury (0.3g., 1.3m.mol.) was added to a stirred suspension of cis-$(Ph_3P)(CO)PtCl_2$ (0.63g., 1.1m.mol.) in benzene (35 ml.) The solution became clear after 2 hours at room temperature. Stirring was continued overnight after which a small deposit of metal was filtered off and solvent was removed under reduced pressure. The white residue was heated at 70°/0.5m.m. and methylmercuric chloride (0.28g., 70%) was obtained as a white crystalline sublimate. The residue contained unchanged starting material ν(CO)2090cm^{-1} and product ν(CO)1665cm^{-1}. Repeated washing of the product with small volumes of chloroform removed most of the unchanged $(Ph_3P)(CO)PtCl_2$ and left impure di-μ-chlorobistriphenylphosphinediacetyldiplatinum, $(Ph_3P)_2Pt_2(COMe)_2Cl_2$, (0.2g., 38%) m.p. 260° (dec) [Found: C, 46.15; H, 4.1%; M(mass spectrum)1070. $C_{40}H_{36}Cl_2O_2P_2Pt_2$ requires C, 44.85; H, 3.4%; M, 1071.7.] Mass spectral data are given in table 10.

cis-tri-n-butylphosphinecarbonylplatinum II chloride and diphenylmercury

Diphenylmercury (0.36g., 1m.mol.) was added to a solution of cis-$(Bu_3P)(CO)PtCl_2$(0.39g., 1m.mol.) in

TABLE 9

Mass Spectral data for $(Ph_3P)_2Pt_2(COMe)_2Cl_2$

ION	POSSIBLE FRAGMENT	M*	PROBABLE PROCESS
1170	molecular ion	479	535 ⟶ 507 (+ CO)
790		466	520 ⟶ 492 (+ CO)
756		450	570 ⟶ 507 (+COCl)
729		423	492 ⟶ 456 (+ HCl)
720	$(Ph_3P)_2Pt$	313	456 ⟶ 378 ($+C_6H_6$)
678			
658			
570	$(Ph_3P)Pt(COMe)Cl_2$		
520	$(Ph_3P)PtCOCl$		
507	$(Ph_3P)PtMeCl$		
492	$(Ph_3P)PtCl$		
456	$(Ph_3P)PtCl-HCl$		
394			
378	$456 - C_6H_6$		
262	Ph_3P		

TABLE 10

Mass spectral data for $(Ph_3P)_2Pt_2(COPh)_2Cl_2$

ION	POSSIBLE FRAGMENT	M*	PROBABLE PROCESS
1130	$(Ph_3P)_2Pt_2Ph_2Cl_2$	499	569 ⟶ 532 (+ HCl)
		314	457 ⟶ 378 ($+C_6H_6$)
673	$(Ph_3P)PtPh(COPh)Cl$		
638	$(Ph_3P)PtPh(COPh)$		
610	$(Ph_3P)PtPh_2$		
569	$(Ph_3P)PtPhCl$		
532	$(Ph_3P)PtPhCl-HCl$		
457	$(Ph_3P)Pt$		
262	Ph_3P		

benzene (25 ml.) The mixture turned yellow and was stirred for 1½ hours. The volume was reduced and a precipitate of phenylmercuric chloride (0.26g., 73%) was filtered off. Solvent was removed and the residue was briefly heated at 80°/0.5m.m.Hg to remove final traces of PhHgCl. The residue was recrystallised from light petroleum (b.p. 40-60°) - benzene to give light yellow crystals of di-μ-chloro-bistri-n-butylphosphinebis-benzoyldiplatinum, $(Bu_3P)_2Pt_2(COPh)_2Cl_2$, (0.25g., 51%) m.p. 142-144° (dec). (Found: C, 42.25; H, 6.05%. $C_{35}H_{64}Cl_2O_2P_2Pt_2$ requires C, 42.35; H, 6.0%).

cis-tri-n-butylphosphinecarbonylplatinum II chloride and dimethylmercury

Dimethylmercury (0.3g., 1.3m.mol.) was added to a solution of cis-$(Bu_3P)(CO)PtCl_2$ (0.49g., 1m.mol.) in benzene (25 ml.) and the mixture was stirred for 5 hours. A small deposit of metal was filtered off, and the solvent was removed under reduced pressure. The oily residue was heated at 40°/0.05m.m.Hg and methylmercuric chloride (0.27g., 67%) was sublimed off. The residue consisted of an almost colourless oil showing carbonyl absorption at 1665cm^{-1}.

cis-triphenylphosphinecarbonylplatinum II chloride and methyllithium

Methyl lithium in ether (1.2 ml., 1.95M.) was added to a

suspension of cis-$(Ph_3P)(CO)PtCl_2$ (1.1g., 2m.mol.) in benzene. The solution turned yellow and was stirred for 1½ hours. Water was added and the organic layer was separated and dried over $MgSO_4$. Removal of solvent left a yellow solid mixture which showed carbonyl absorption at 2090, 2045 and 2020cm^{-1}, due respectively to $(Ph_3P)(CO)PtCl_2$, $(Ph_3P)(CO)MePtCl$ and $(Ph_3P)(CO)PtMe_2$.

cis-tri-n-butylphosphinecarbonylplatinum II chloride and methyl lithium

In an experiment similar to the above, an excess of methyl lithium was added to cis-$(Bu_3P)(CO)PtCl_2$. The only product was a brown oil with carbonyl absorption at 2030cm^{-1} thought to be tri-n-butylphosphinecarbonyl-dimethylplatinum.

cis-tri-n-butylphosphinecarbonylplatinum II chloride and phenylmagnesium bromide

Phenylmagnesium bromide, prepared from bromobenzene (0.63g., 4.2m.mol.) and magnesium (0.1g., 4.2m.mol.) in ether (5 ml.), was added to a solution of cis-$(Bu_3P)(CO)PtCl_2$ (0.44g., 0.9m.mol.) in benzene (20 ml.) The mixture was stirred for 1 hour during which time a brown colour developed. Dilute hydrochloric acid was added to the mixture and the organic layer was treated in the usual way to yield a brown oil. Its smell and i.r. spectrum ν(CO) 1662cm^{-1} indicated the presence of benzophenone.

Light petroleum (b.p. 40-60°) (5 ml.) was added to the mixture and a precipitate of the complex $(Bu_3P)_2Pt_2(COPh)_2Br_2$ was produced (60mg., 12%) m.p. 160-170° (dec). (Found: C, 37.65; H, 6.0%. $C_{38}H_{64}Br_2O_2P_2Pt_2$ requires C, 39.1; H, 5.55%).

The oily residue showed carbonyl absorption at 2060cm^{-1} $(Bu_3P)(CO)PtPh_2$, 1980 and 1745cm^{-1}.

<u>trans-bistriphenylphosphinecarbonyliridium I chloride and diphenylmercury</u>

trans-$(Ph_3P)_2(CO)IrCl$ (117mg., 0.15m.mol.) was dissolved in benzene (50 ml.) and diphenylmercury (58mg., 0.015m.mol.) was added. The solution was stirred at room temperature for 24 hours and solvent was removed. The yellow residue was recrystallised from toluene/hexane to yield light yellow crystals of $(Ph_3P)_2(CO)ClIr(HgPh)Ph$.

CHAPTER TWO

CYCLOPENTADIENYL COMPLEXES OF THE NICKEL GROUP.

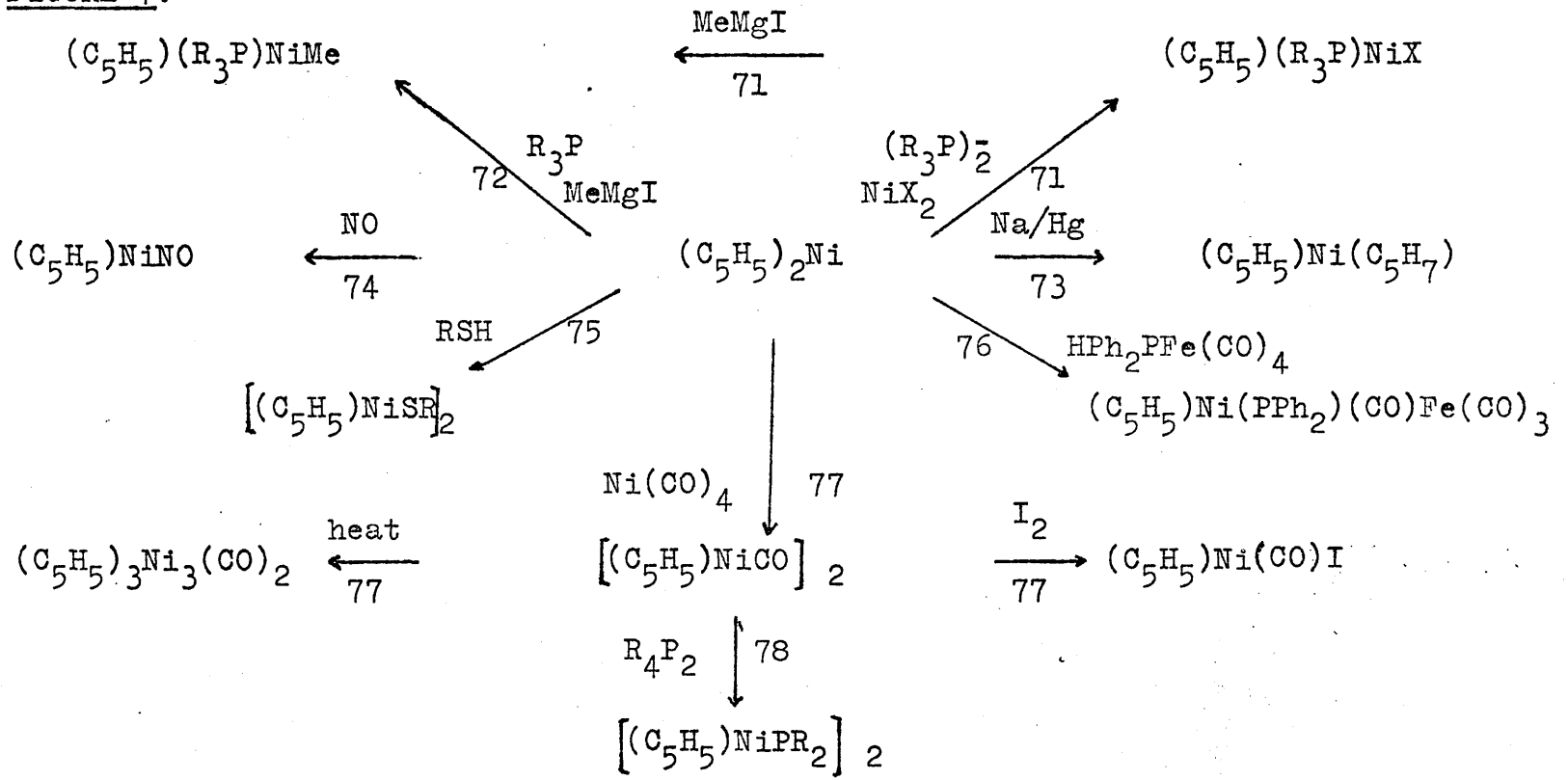
CHAPTER TWO

Introduction.

In common with almost all the other transition metals the nickel group forms a number of cyclopentadienyl-metal complexes, by far the greatest number of these being derivatives of nickel itself. One reason for this is that a nickel compound containing cyclopentadienyl groups, $(\pi\text{-}C_5H_5)_2Ni$, is readily available, and figure 7 exemplifies the variety of ways in which nickelocene has been transformed into different derivatives. In all these complexes the cyclopentadienyl group is π-bonded to nickel. An X-ray structural investigation of $(C_5H_5)(Ph_3P)NiPh$ has shown[79] that the nickel atom is in a pseudo-pentacoordinate environment, being bonded to a triphenylphosphine group, a σ-phenyl group and a formally tridentate π-cyclopentadienyl ring which undergoes substantial thermal motion. The average nickel-(π-cyclopentadienyl) carbon distance is 2.139Å.

Organonickel halides of the type $(\pi\text{-}C_5H_5)(R_3P)NiX$ (X = halogen) were first described in the literature in 1962 as a result of investigations of Schroll[80] and Schropp.[81] Schroll's procedure, the more straightforward

FIGURE 7.



Reactions of nickelocene

of the two methods, involved a disproportionation reaction between $(\pi\text{-}C_5H_5)_2Ni$ and $(Ph_3P)_2NiCl_2$ in a refluxing inert solvent. This type of reaction has since been successfully repeated using different phosphines and polar solvents, such as T.H.F.

$$(R_3P)_2NiX_2 + (\pi\text{-}C_5H_5)_2Ni \longrightarrow 2(\pi\text{-}C_5H_5)(R_3P)NiX$$

Other methods of preparation include the reactions between $(\pi\text{-}C_5H_5)_2Ni$, $Ni(CO)_4$, I_2 and R_3P;[71] between $(\pi\text{-}C_5H_5)_2Ni$ and Ph_3PHCl[82] and between $(\pi\text{-}C_5H_5)_2Ni$, R_3P and CCl_4.[83] The complexes of this type are stable in air, both in the solid state and in solution. σ-Bonded organic substituents can then be introduced by treatment of the $(\pi\text{-}C_5H_5)(R_3P)NiX$ complexes with Grignard or organolithium reagents. Some of the $(\pi\text{-}C_5H_5)(R_3P)NiR^1$ compounds are also reported to be air-stable solids.[71]

The disproportionation reaction above cannot be applied to palladium or platinum chemistry for two reasons. Firstly, no equivalent to nickelocene is known for these elements; and secondly, tertiary phosphines are more strongly held by these metals in complexes of the type $(R_3P)_2MX_2$, and the elimination of a phosphine in solution is a necessary step in the disproportionation reactions in order to initiate nucleophilic attack at nickel

(vide ultra).

The cyclopentadienyl complexes of palladium and platinum which are known, and their methods of preparation, are listed in table 11. All are derivatives of the metals in the +2 state with the exception of $(\pi\text{-}C_5H_5)PtMe_3$ and possibly $(\pi\text{-}C_5H_5)MNO$ (M = Pd, Pt). The platinum IV complex, $(\pi\text{-}C_5H_5)PtMe_3$, is remarkable in its stability, being a white crystalline compound which sublimes unchanged in vacuum at ca.60°. An X-ray structure of this complex shows[96] that the cyclopentadienyl ring is symmetrically π-bonded with an average Pt-(π-cyclopentadienyl) carbon distance of 2.20Å.

Many of the cyclopentadienyl palladium and platinum derivatives have been prepared under exacting conditions and in small yield compared with their nickel analogues, e.g. $(C_5H_5)PdNO$, $[(C_5H_5)Pt(CO)]_2$, and most of the others have been synthesised in studies which were concerned with the other organic ligands bonded to the metal, e.g. $(\pi\text{-}C_5H_5)PdC_{10}H_{12}OMe$, $[(\pi\text{-}C_5H_5)PtC_8H_{12}]^+BF_4^-$. The result of this is that few comparative studies have been made. The only complex whose reactions have been thoroughly investigated in fact has been the palladium compound $(\pi\text{-}C_5H_5)Pd(\pi\text{-allyl})$. It was found[97] that

TABLE 11. CYCLOPENTADIENYL COMPLEXES OF PALLADIUM AND PLATINUM.

COMPLEX	METHOD OF PREPARATION	REF.
$(C_5H_5)PdNO$	$PdCl_2 + NO \longrightarrow$ 'PdNOCl' $\xrightarrow{NaC_5H_5}$	84
$(C_5H_5)PdC_3H_5$	$[PdCl(C_3H_5)]_2 + 2NaC_5H_5$	85
$(C_5H_5)PdC_6H_9$	$[PdCl(C_6H_9)]_2 + 2NaC_5H_5$	86
$(C_5H_5)PdC_{10}H_{12}OMe$	$(C_{10}H_{12}OMePdCl)_2 + 2NaC_5H_5$	87
	$+ 2TlC_5H_5$	88
$(C_5H_5)PdC_4Ph_4H_2OH$ $(C_5H_5)PdC_4Ph_4H_2OMe$ $(C_5H_5)PdC_4Ph_4H_2OEt$	$[(C_5H_5)PdC_4Ph_4]Br + OR^-$	89
$[(C_5H_5)PdC_8H_{12}]BF_4$	$(C_5H_5)PdC_8H_{12}OMe + Ph_3C^+BF_4^-$	90
$[(C_5H_5)PdC_4Ph_4]Br$	$[(C_5H_5)PdC_4Ph_4]FeBr_4 + K_4Fe(CN)_6$	89
$[(C_5H_5)PdC_4Ph_4]FeBr_4$	$[(C_5H_5)Fe(CO)_2]_2 + Ph_4C_4PdBr_2$	89
$[(C_5H_5)PdC_8H_{12}]FeBr_4$	$[(C_5H_5)Fe(CO)_2]_2 + (C_8H_{12})PdBr_2$	89
$(C_5H_5)PtNO$	$Pt_2(CO)_2Cl_4 + NO + NaC_5H_5$	91
$(C_5H_5)PtC_3H_5$	$(CH_3CH=CH_2)PtCl_2 +$ allyl MgBr $+ NaC_5H_5$	86
$(C_5H_5)PtC_8H_{12}OMe$	$(C_8H_{12}OMePtCl)_2 + 2(C_5H_5)Tl$	88
$(C_5H_5)PtC_{10}H_{12}OMe$	$(C_{10}H_{12}OMePtCl)_2 + 2(C_5H_5)Tl$	88
$[(C_5H_5)Pt(CO)]_2$	$PtCl_2 + CO \longrightarrow$ 'Pt(CO)$_2$Cl$_2$' $\xrightarrow{NaC_5H_5}$	92
$(C_5H_5)Pt(CO)I$	$[(C_5H_5)Pt(CO)]_2 + I_2$	92
$C_{20}H_{20}Pt_2$	$PtCl_2 + 3NaC_5H_5$	93
$(C_5H_5)PtMe_3$	$Me_3PtI + NaC_5H_5$	94
$[(C_5H_5)PtC_8H_{12}]BF_4$	$(C_5H_5)Pt(C_8H_{12}OMe) + Ph_3C^+BF_4^-$	90

treatment of this species with either electrophilic or nucleophilic reagents in acid, neutral, or basic media results in rapid cleavage of the cyclopentadienyl ligand, indicating that the π-allyl ligand is more strongly bound than the cyclopentadienyl moiety.

Few comparisons can be made between analogous nickel, palladium and platinum derivatives, but the series (π-C_5H_5)MNO(M = Ni,[74] Pd,[84] Pt[91]) does show that the palladium and platinum complexes are no less stable than their nickel counterpart. Indeed, in some cases the heavier metal analogues are more stable. Thus, $(C_5H_5)Ni(CO)I$ is very sensitive towards air and moisture[77] and decomposes above 20°, whereas $(C_5H_5)Pt(CO)I$ is reasonably air stable and has a melting point of 55°. It appears, therefore, that it is only the lack of suitable synthetic routes which has till now prevented the preparation of a wider range of palladium and platinum derivatives, rather than any inherent instability of the compounds.

In almost all the cyclopentadienyl complexes of nickel, palladium and platinum described so far the organic ligand has been π-bonded to the metal

The cis- and trans-isomers of $(Me_2S)_2Pt(C_5H_5)_2$ have

been reported[95] to be σ-bonded but are unstable above 0°C. σ-Cyclopentadienyl derivatives of transition metals are well established and it is surprising that stable derivatives of this type have not previously been isolated for platinum, considering the relatively high stability of complex alkyl and aryl derivatives of platinum II.[25]

In most cases, the reagent used to introduce the cyclopentadienyl ligand into the palladium and platinum complexes has been sodium cyclopentadienide. This ionic compound is best prepared by adding cyclopentadiene in T.H.F. to a dispersion of sodium sand in xylene. A reddish-purple solution is immediately produced.

$$3\ C_5H_6 + 2Na \longrightarrow 2\ C_5H_5Na + C_5H_8$$

Cyclopentadienyl thallium has also been successfully utilised as a cyclopentadienylating agent. This complex is prepared by treatment of thallous sulphate in NaOH with cyclopentadiene.

$$Tl_2SO_4 + C_5H_6 + NaOH \longrightarrow (C_5H_5)Tl + Na_2SO_4 + H_2O$$

The most striking property of this light yellow, crystalline material is its remarkable stability, particularly towards hydrolysis and oxidation. It readily sublimes in vacuum (80°/0.5mmHg) and darkens

only slowly on exposure to air and light. Cyclopentadienyl thallium is, therefore, found to offer the following advantages over sodium cyclopentadienide:-

(1) $(C_5H_5)Tl$ is air stable and readily obtained in the pure state.

(2) $(C_5H_5)Tl$ undergoes fewer side reactions in certain transition metal systems than $Na\ C_5H_5$.

(3) The by-product TlX is insoluble and simply removed.

The structure and bonding in this complex are thus of interest and much work has been done in this area in recent years. Electron diffraction,[98] infrared[99] and microwave[100] studies have established the structure of the gaseous compound. In the vapour phase, $(C_5H_5)Tl$ exists as a half-sandwich structure with the thallium atom situated centrally above the cyclopentadienyl ring (C_{5v} point group). The nature of the bonding in this complex is, however, still not clear. The metal-ring bond length, 2.41Å, together with chemical evidence and estimates of overlap integrals,[99] indicates a considerable degree of ionic character in the bond. Nevertheless, more recent calculations of the overlap integrals support predominantly covalent bonding in the complex.[98]

The structure of the crystalline compound has been

established by X-ray diffraction.[101] The crystal is characterised by infinite zig-zag chains made up of alternate thallium atoms and cyclopentadienyl rings. The ring-metal distance in the crystal, 3.19Å, is considerably larger than that in the vapour. Recently, a study of the infrared and laser Raman spectra of crystalline (polymeric) $(C_5H_5)Tl$ has been reported.[102] The vibrational spectra were found to support predominantly ionic bonding in the complex, although there was evidence for some covalent character in the bonding.

In view of our work with organomercurials, we were interested in determining whether dicyclopentadienyl mercury could also be used to add the cyclopentadienyl group to nickel, palladium and platinum compounds.

Dicyclopentadienylmercury was first reported in 1956 by Piper and Wilkinson.[103] It is a light yellow crystalline solid when pure but is unstable, decomposing to form the metal on exposure to air or light. On the basis of its infrared spectrum and chemical behaviour the original authors considered it to have σ-bonded cyclopentadienyl rings. The observation of a single proton resonance at ca.4τ was rationalised in terms of

the σ-bonded structure by postulating that rapid shifting of the mercury-carbon bond among the five possible positions was occurring, making all the cyclopentadienyl protons equivalent. However, at temperatures as low as -70°, in a number of solvents, no significant changes in the ^{1}H n.m.r. spectrum of $(C_5H_5)_2Hg$ and $(C_5H_5)HgCl$ occur and Russian workers have argued[104] that the cyclopentadienyl rings in these complexes are π-bonded. The controversy has recently been resolved by a study[105] of the n.m.r. spectra of the compounds C_5H_5HgX (X = Cl,Br,I and C_5H_5) in various ethereal solvents over the temperature range -140° to + 120°. The spectra, of the AA'BB'C type at low temperatures, are consistent with the C_5H_5 group being fluxional with a nuclear configuration of lowest free energy in which the C_5H_5 moiety is σ-bonded to the mercury atom. It was found that the less electronegative the second substituent on the mercury atom was, the more facile was the intramolecular 'ring-whizzing' i.e. $(C_5H_5)_2Hg > C_5H_5HgI > C_5H_5HgBr > C_5H_5HgCl$. Although the nature of bonding in $(C_5H_5)_2Hg$ has been thoroughly investigated, its reactions with transition metal complexes have been

neglected. In this work we have studied some of its reactions with the nickel group metals. The reactions of cyclopentadienyl thallium with complexes of these metals have also been extensively examined.

In the first section of this chapter, studies on some nickel cyclopentadienyl complexes are described. Data on the palladium and platinum series are recorded in section 2.

SECTION 1. Cyclopentadienyls of Nickel.

1) Preparation and reactions of complexes.

We find that both C_5H_5Tl and $(C_5H_5)_2Hg$ react with the nickel complexes $(R_3P)_2NiCl_2$ (R = Et,Ph) to produce a π-cyclopentadienyl-containing product.

$$(Et_3P)_2NiCl_2 + C_5H_5Tl \longrightarrow (\pi\text{-}C_5H_5)(Et_3P)NiCl + Et_3P + TlCl$$

$$2(Ph_3P)_2NiCl_2 + (C_5H_5)_2Hg \longrightarrow 2(\pi\text{-}C_5H_5)(Ph_3P)NiCl + (Ph_3P)_2HgCl_2$$

These reactions are performed in T.H.F. and are complete within 1 hour at room temperature. The latter reaction probably produces C_5H_5HgCl, which will react with the eliminated phosphine.

$$2C_5H_5HgCl + 2Ph_3P \longrightarrow (C_5H_5)_2Hg + (Ph_3P)_2HgCl_2$$

The complexes, $(\pi\text{-}C_5H_5)(R_3P)NiCl$, are produced in rather poor yield by these methods, possibly because the products can further react with the cyclopentadienylating reagent. Thus, with excess C_5H_5Tl the reactions proceed further to yield a mixture of nickelocene and tertiary phosphine.

$$(\pi\text{-}C_5H_5)(Ph_3P)NiCl + C_5H_5Tl \longrightarrow (\pi\text{-}C_5H_5)_2Ni + Ph_3P + TlCl$$

Exchange reactions between nickelocene and various nucleophiles have been examined[83] by Russian workers, and we have extended the range of reactions by reacting $(\pi\text{-}C_5H_5)_2Ni$ with mercurials, in the presence of the

nucleophile triphenylphosphine.

$$(\pi\text{-}C_5H_5)_2Ni + Ph_3P + Me_2Hg \longrightarrow (\pi\text{-}C_5H_5)(Ph_3P)NiMe + C_5H_5HgMe$$

$$2(\pi\text{-}C_5H_5)_2Ni + (Ph_3P)_2HgCl_2 \longrightarrow 2(\pi\text{-}C_5H_5)(Ph_3P)NiCl + (C_5H_5)_2Hg$$

These reactions were performed in deuterobenzene on a small scale and the formation of products was observed by n.m.r. spectroscopy. In both cases, reaction was complete within a few hours.

The second equation demonstrates that $(C_5H_5)_2Hg$ does not react with $(\pi\text{-}C_5H_5)(R_3P)NiCl$ compounds, and we also find that no reaction is apparent between $(\pi\text{-}C_5H_5)(R_3P)NiX$ and Me_2Hg after 5 days.

2) Mechanisms of the reactions.

There is evidence that a common mechanism operates in all the reactions which we have described involving nickelocene. The critical step appears to be nucleophilic attack by a neutral ligand at nickelocene, converting a π-bonded cyclopentadienyl to a σ-bonded group.

$$(\pi\text{-}C_5H_5)_2Ni + R_3P \longrightarrow (\pi\text{-}C_5H_5)(R_3P)Ni(\sigma\text{-}C_5H_5)$$

The equilibrium must lie well to the left since no cyclopentadienyl containing species are observed in the n.m.r. when equimolar amounts of $(\pi\text{-}C_5H_5)_2Ni$ and Ph_3P are mixed in C_6D_6. The complex containing both

π - and σ-bonded rings should give a spectrum since it is diamagnetic, unlike nickelocene itself. Further evidence as to the position of equilibrium is given by the reaction between $(\pi\text{-}C_5H_5)(R_3P)NiCl$ and C_5H_5Tl. The first step must involve formation of the $(\pi\text{-}C_5H_5)(R_3P)Ni(\sigma\text{-}C_5H_5)$ species which rapidly eliminates the phosphine to give $(\pi\text{-}C_5H_5)_2Ni$.

In the absence of any other species, the reaction between nickelocene and a phosphine slowly proceeds to $(R_3P)_4Ni$ and $C_{10}H_{10}$, presumably by a further nucleophile induced $\pi \longrightarrow \sigma$ conversion of the cyclopentadienyl group, followed by reductive elimination from the unstable σ-bonded species. If the reaction is performed in the presence of a covalent compound cleavage of the unstable $Ni\text{-}(\sigma\text{-}C_5H_5)$ bond readily occurs. Thus, we find that if $(\pi\text{-}C_5H_5)_2Ni$ and Ph_3P are mixed in $CDCl_3$ the green solution turns to red and signals corresponding to $(\pi\text{-}C_5H_5)(Ph_3P)NiCl$ are detected in the n.m.r. spectrum. The initial formation of the unstable σ-bonded species is supported by this observation since chloroform is known to cleave metal-carbon σ-bonds to yield the corresponding metal-chlorine compound. For example, it reacts with $(\pi\text{-}C_5H_5)(Ph_3P)NiMe$.[106] The reaction which we observe

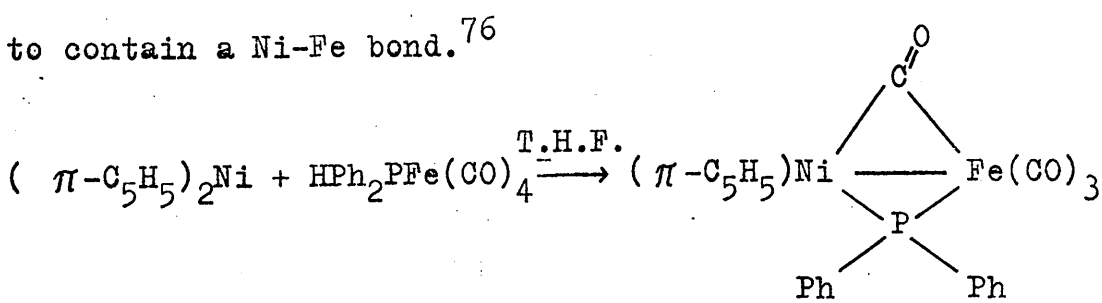
between $(\pi\text{-}C_5H_5)_2Ni$, Ph_3P and Me_2Hg can also be rationalised on the basis of cleavage of the Ni-($\sigma\text{-}C_5H_5$) bond to give $(C_5H_5)HgMe$ with concurrent formation of the Ni-Me containing species.

A necessary condition for these reactions to occur is the initial nucleophilic attack by the phosphine at nickel. Thus, the mercury-phosphorus bonds in $(Ph_3P)_2HgCl_2$ must be sufficiently weak to allow triphenylphosphine to be eliminated in solution and to attack $(\pi\text{-}C_5H_5)_2Ni$. The course of this reaction is then the same as before, $(\pi\text{-}C_5H_5)(Ph_3P)NiCl$ being formed. A similar mechanism is also likely to operate in the reaction between nickelocene and the bisphosphine-nickel II halide compounds.

This led us to believe that a possible route to $(\pi\text{-}C_5H_5)(R_3P)MX$ (M = Pd,Pt) complexes might be to react nickelocene with the $(R_3P)_2MX_2$ species. No reaction was observed, however, when these complexes were stirred together in refluxing solvent. We conclude that this is accounted for by the fact that tertiary phosphines are more strongly held by palladium and platinum, in complexes of the type $(R_3P)_2MX_2$, than they are held by either nickel or mercury.

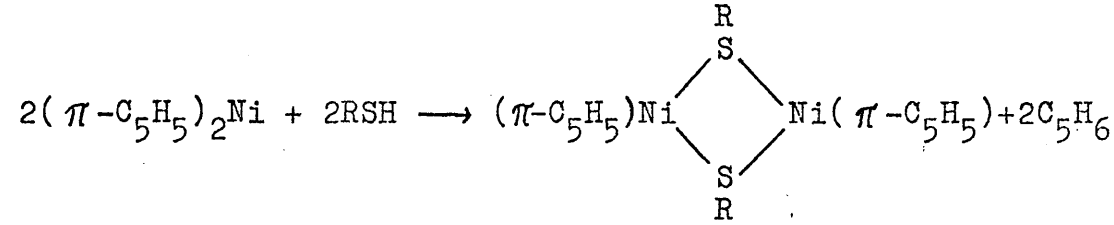
The mechanism which we have invoked to rationalise our results may also be utilised to account for the products of some reactions which have only been briefly described in the literature. Japanese workers have reported[107] that the reaction between 1 mole of (π-C_5H_5)Ni, 2 moles of Bu_3P and 1 mole of CH_2 = CH-CH_2Cl produces the salt $[(\pi\text{-}C_5H_5)Ni(PBu_3)_2]Cl$(I). No details of the organic by-product or the possible mechanism were given. Salts of type (I) are well known and are formed by the reaction of equimolar quantities of R_3P and (π-C_5H_5)(R_3P)NiX.[108] In the case under consideration we may imagine (π-C_5H_5)(Bu_3P)NiCl(II) to be an intermediate which reacts with excess Bu_3P to give (I) Initial nucleophilic attack of Bu_3P on nickelocene and cleavage of the Ni-(σ-C_5H_5) bond by the covalent halide CH_2 = CH-CH_2Cl would account for compound (II) being the intermediate.

Another compound prepared from nickelocene is thought to contain a Ni-Fe bond.[76]



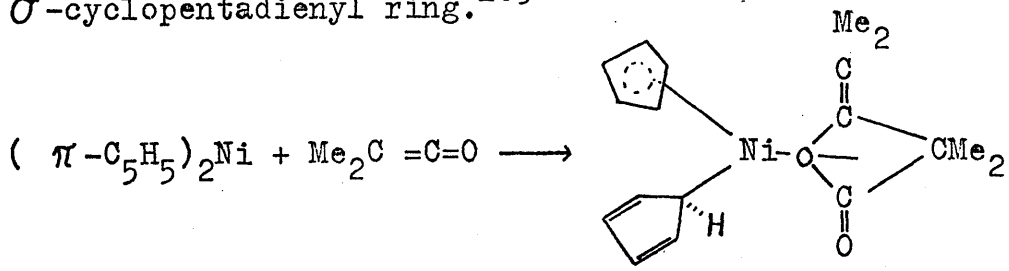
The first stage in this reaction presumably also involves attack of the phosphorus atom at nickel with concurrent or subsequent elimination of cyclopentadiene.

Thiols can also act as nucleophiles, since Schropp has shown[75] that nickelocene reacts with thiols in benzene to produce binuclear derivatives.



[R = Me, Et.]

Very recently, support has been given to the proposed mechanism for these reactions, by the isolation of a stable nickel compound containing both a π- and a σ-cyclopentadienyl ring.[109]



SECTION 2. Cyclopentadienyls of Palladium and Platinum

1. Preparation of the complexes.

(a) (π-C_5H_5)(R_3P)ML (M = Pd,Pt; L = halogen or organic substituent)

Bridge-splitting reactions of cyclopentadienyl thallium have previously been shown to produce π-cyclopentadienyl derivatives of transition metals.[88] We have utilised a similar procedure to form the hitherto unknown palladium and platinum complexes, (π-C_5H_5)(R_3P)ML.

Binuclear halogen-bridged palladium compounds $(Et_3P)_2Pd_2X_4$ (X = Cl,Br,I) react with a suspension of cyclopentadienyl thallium in T.H.F. at room temperature.

$$(Et_3P)_2Pd_2X_4 + 2\ C_5H_5Tl \longrightarrow 2(\ \pi\text{-}C_5H_5)(Et_3P)PdX + 2TlX$$

Reaction is complete in 30 minutes. After filtering off the insoluble thallous halide, the solvent is removed and the residue recrystallised from a benzene-hexane mixture to yield dark green needles of the required complex in about 80% yield. The compounds were characterised by elemental analysis, n.m.r., i.r. and mass spectra. They appear to be indefinitely stable to aerial oxidation when pure but gradually decompose in solution or in the impure solid state when exposed to air. Good yields are also obtained from the tri-isopropylphosphine complex $(Pr^i_3P)_2Pd_2Br_4$ but the

yield is reduced when triphenylphosphine is used as a neutral ligand. The low solubility of the starting material in the latter case may account for this.

Reactions between cyclopentadienyl thallium and analogous platinum complexes have proved to be less successful. Although the binuclear derivative $(Et_3P)_2Pt_2I_4$ reacts with C_5H_5Tl to produce dark orange crystals of $(\pi\text{-}C_5H_5)(Et_3P)PtI$, the yields are less than 20%. The compound, like its palladium analogues is indefinitely stable in air. Competing side reactions may be the cause of the low yield in this case since a yellow unstable solid, possibly a platinum (0) derivative, is also formed. In addition to this we isolated, in less than 1% yield, orange crystals of another cyclopentadienyl-containing species. The presence of the cyclopentadienyl ligand in this complex was shown by infrared analysis (see table 18) and since 12 peaks associated with vibrations of the C_5H_5 group were detected, metal-carbon σ-bonding was indicated. The highest peak in the mass spectrum of the compound was observed at 880 ± 5, and showed the expected pattern for two platinum atoms in the same species. The peak is most likely due to $(Et_3P)_2Pt_2I_2^+$ (M = 880). The most abundant peak in the spectrum, however, was at 505 corresponding to $(C_5H_5)(Et_3P)PtI^+$

On the basis of these observations, we suggest that the complex may be formulated as $(Et_3P)_2Pt_2(\sigma\text{-}C_5H_5)_2I_2$, i.e. a binuclear derivative with bridging iodide groups and terminal phosphine and σ-cyclopentadienyl ligands. The predominant breakdown pathway in the mass spectrometer is bridge-splitting, with loss of the terminal C_5H_5 groups, to form $(Et_3P)_2Pt_2I_2^+$ being a minor process. In support of this, the mass spectrum of $(Et_3P)_2Pt_2Ph_2Br_2$ showed the ion $(Et_3P)PtPhBr^+$ in large abundance.

The place of cyclopentadienyl thallium in these reactions can be taken by dicyclopentadienyl mercury. Thus, an n.m.r. examination of mixed solutions of $(Et_3P)_2Pt_2I_4$ and $(C_5H_5)_2Hg$, and $(Et_3P)_2Pt_2Br_4$ and $(C_5H_5)_2Hg$ showed that the reactions had proceeded to give $(\pi\text{-}C_5H_5)(Et_3P)PtX$ and C_5H_5HgX. Cyclopentadienylmercury derivatives are unstable in solution, however, and the mixtures gradually degraded. This decomposition prohibits the use of $(C_5H_5)_2Hg$ in large scale preparations of the metal π-cyclopentadienyl compounds. As was found with diphenylmercury, reactions of C_5H_5Tl or $(C_5H_5)_2Hg$ with the chloride $(Et_3P)_2Pt_2Cl_4$ led only to decomposition products.

The reaction between (π-C_5H_5)(Et_3P)PdBr and phenylmagnesium bromide led to formation of the organic derivative (π-C_5H_5)(Et_3P)PdPh. This complex was isolated as a yellow liquid and identified by its n.m.r. and i.r. spectra. Attempted purification by distillation under vacuum (50°/0.1mmHg) led only to decomposition, biphenyl being a major product.

Similar platinum complexes can be prepared in almost quantitative yield by the action of cyclopentadienyl thallium on halogen-bridged organoplatinum compounds.

$$(R_3P)_2Pt_2X_2R^1_2 + 2\ C_5H_5Tl \longrightarrow 2(\pi\text{-}C_5H_5)(R_3P)PtR^1 + 2TlX$$

In these reactions, good yields (ca.80%) are obtained for X = Cl, Br or I; R = Et, Bu^n and R^1 = Ph, o-tolyl and COPh. The products are yellow liquids which decompose only slowly in air, and they can be purified by vacuum distillation (70°/0.1mmHg). Comparable organopalladium starting materials are not known with the result that this route is not available for palladium derivatives.

It is interesting to note that the organoplatinum complexes (π-C_5H_5)(R_3P)PtR^1 are obtained in good yield, whereas their halogen analogues cannot be prepared for X = Cl or Br and are only formed in small yield for X = I. It is probable that a different mechanism of formation operates for each case.

A bridge-splitting mechanism must operate in the reaction between $[(C_8H_{12}OMe)PtCl]_2$ and C_5H_5Tl to produce $(C_8H_{12}OMe)Pt(\pi\text{-}C_5H_5)$[88] and such a mechanism could explain the formation of $(\pi\text{-}C_5H_5)(R_3P)PtR^1$ from $(R_3P)_2Pt_2R_2^1X_2$ and C_5H_5Tl.

Isolation of the σ-cyclopentadienyl complex $(Et_3P)_2Pt_2(\sigma\text{-}C_5H_5)_2I_2$ provides an important clue to the mechanism of the reaction between $(Et_3P)_2Pt_2X_4$ (X = halogen) and C_5H_5Tl in that it indicates that terminal halogen substitution rather than bridge-splitting is the initial step. Further evidence is provided by the fact that when the reaction between $(Et_3P)_2Pt_2Br_4$ and C_5H_5Tl is performed in benzene, the ^1H n.m.r. spectrum of the product is complex in the region between τ 3.4 and τ 4.2 indicative of a mixture of σ- and π-bonded C_5H_5 complexes. No evidence for cyclopentadienyl-platinum derivatives was detected in the reaction between $(Et_3P)_2Pt_2Cl_4$ and C_5H_5Tl, but this is not surprising in view of the fact that reactions between this platinum complex and Grignard or organomercurial reagents also lead to decomposition.

In view of these observations, treatment of the $(Et_3P)_2Pt_2X_4$ compounds with C_5H_5Tl is thought to produce $(Et_3P)_2Pt_2(\sigma\text{-}C_5H_5)_2X_2$ initially. For X = Cl or Br,

decomposition of this species, possibly by a free radical mechanism, must occur readily. When the halogen ligand is I^- the complex is sufficiently stable to be isolated. The bulk of the $(Et_3P)_2Pt_2(\sigma\text{-}C_5H_5)_2I_2$ formed, however, must either decompose to form the yellow Pt(0) derivative or undergo $\sigma \longrightarrow \pi$ conversion of the C_5H_5 ligand to yield $(\pi\text{-}C_5H_5)(Et_3P)PtI$.

The mechanism of formation of the analogous palladium complexes may be similar to this, but the reason why these derivatives are isolated in good yield for X = Cl, Br or I, is not yet understood.

(b) $\underline{[(\pi\text{-}C_5H_5)(Et_3P)_2M]^+X^-}$ $\underline{(M = Pd,Pt;\ X = Br,ClO_4)}$

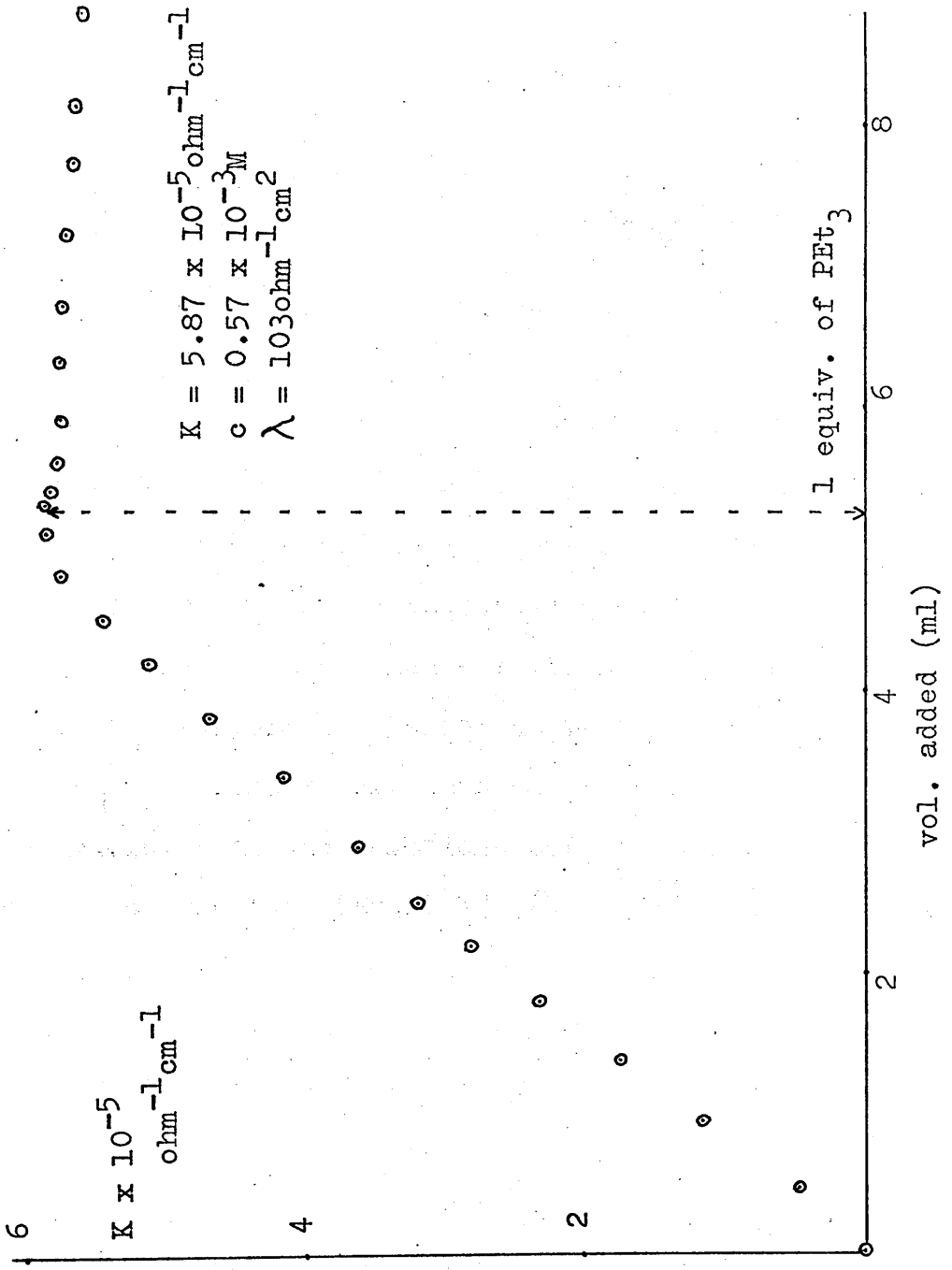
In section 1 of this chapter we noted that excess phosphine can promote $\pi \longrightarrow \sigma$ conversion of cyclopentadienyl groups bonded to nickel, the σ-cyclopentadienyl complexes being too unstable to isolate. We were interested in reacting π-cyclopentadienyl palladium and platinum derivatives with neutral ligands, since it seemed probable that σ-bonded cyclopentadienyls of these metals would be more stable than those of nickel. There appeared to be, therefore, possibilities of greatly extending knowledge about C_5H_5 compounds of the nickel group.

Addition of a solution of triethylphosphine in methanol to dilute methanolic solutions of (π-C_5H_5)(Et_3P)PdCl, (π-C_5H_5)(Et_3P)PdI or (π-C_5H_5)(Et_3P)PtI causes the conductivity of the solutions to rise to sharp maxima at 1:1 molar ratios (see figure 8). The values of the equivalent conductances are ca.105ohm^{-1}cm^2, corresponding to 1:1 electrolytes with a large cation and thus establishing the salt-like nature of the products. In benzene solution, red crystals of π-cyclopentadienylbistriethylphosphinepalladium II bromide were isolated from the reaction between (π-C_5H_5)(Et_3P)PdBr and triethylphosphine.

(π-C_5H_5)(Et_3P)PdBr + Et_3P $\longrightarrow$ [(π-C_5H_5)(Et_3P)$_2$Pd] $^+Br^-$

This air-stable complex was characterised by normal methods and is similar in nature to the nickel derivatives prepared by Jellinek.[108]

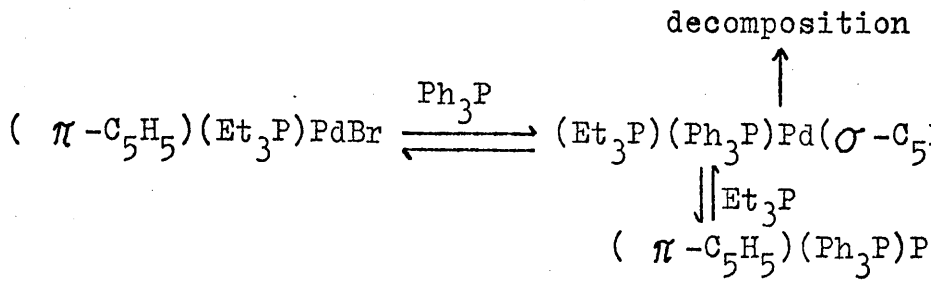
The nature of the tertiary phosphine is important in the formation and stabilisation of the ionic cyclopentadienyls. Thus, although Et_3P reacts with (π-C_5H_5)(Et_3P)PdBr to produce the salt [(π-C_5H_5)(Et_3P)$_2$Pd] $^+Br^-$, no ionic material was detected when Ph_3P was used instead. Signals associated with (π-C_5H_5)(Ph_3P)PdBr and (Et_3P)(Ph_3P)Pd(σ-C_5H_5)Br were observed in the n.m.r. spectra and it appears that a series



Conductimetric titration of (π-C_5H_5)(Et_3P)PdI and PEt_3

FIGURE 8.

of equilibria operate in this case. Decomposition was complete in about 3 hours.



Bubbling carbon monoxide through a solution of $(\pi\text{-}C_5H_5)(Et_3P)PdBr$ had no apparent effect. Possibly an equilibrium similar to the above operates, which lies well to the left. This means that the more basic ligands such as Et_3P support the ionic derivatives.

Ionic π-bonded compounds can also be prepared, in poorer yield, from the reactions between mononuclear complexes of the type $(Et_3P)_2MX_2$ (M = Pd,Pt) and cyclopentadienyl thallium.

$$cis\text{-}(Et_3P)_2PtCl_2 + C_5H_5Tl \longrightarrow [(\pi\text{-}C_5H_5)(Et_3P)_2Pt]^+Cl^- + TlCl$$

In this case the platinum compound proved difficult to crystallise and was, therefore, treated with $NaClO_4.H_2O$ to produce red-brown crystals of $[(\pi\text{-}C_5H_5)(Et_3P)_2Pt]^+(ClO_4)^-$. These reactions are very sensitive to the nature of the solvent and ionic derivatives can only be isolated when polar solvents such as T.H.F. or $CHCl_3$ are used. When benzene is employed, rapid decomposition results.

(c) σ-Cyclopentadienyls of palladium and platinum

The ionic complex $[(\pi\text{-}C_5H_5)(Et_3P)_2Pd]^+Br^-$ is not the only product of the reaction between $(\pi\text{-}C_5H_5)(Et_3P)$-PdBr and Et_3P in benzene. An n.m.r. examination of the supernatant liquid, when the reaction was performed in C_6D_6, showed a small amount of the σ-cyclopentadienyl complex $(Et_3P)_2Pd(\sigma\text{-}C_5H_5)Br$. This could not be isolated and completely decomposed within 1 hour.

Reasonably stable $\sigma\text{-}C_5H_5$ derivatives can be prepared by addition of neutral ligands to some π-cyclopentadienyl platinum complexes.

$(\pi\text{-}C_5H_5)(Et_3P)PtPh + L \longrightarrow (Et_3P)LPt(\sigma\text{-}C_5H_5)Ph$ (L = Et_3P, Ph_3P, CO)

The carbonyl complex, a yellowish liquid, is more stable than the bisphosphine compounds but could not be isolated in the pure state. Carbon monoxide also effects a $\pi \longrightarrow \sigma$ conversion of the cyclopentadienyl group in $(\pi\text{-}C_5H_5)(Et_3P)PtI$ but, as previously noted, does not react with $(\pi\text{-}C_5H_5)(Et_3P)PdBr$.

The formation and isolation of the $\sigma\text{-}C_5H_5$ species, $(Et_3P)(CO)Pt(\sigma\text{-}C_5H_5)Ph$, is interesting since treatment of the nickel complex, $(\pi\text{-}C_5H_5)(Ph_3P)NiPh$, with carbon monoxide at high pressure led only to decomposition products.[71]

$(\pi\text{-}C_5H_5)(Ph_3P)NiPh + CO \longrightarrow (Ph_3P)Ni(CO)_3 + PhC_5H_5$

The first step in this reaction probably involves $\pi \longrightarrow \sigma$ conversion of the coordinated C_5H_5 ligand to give $(Ph_3P)(CO)Ni(\sigma\text{-}C_5H_5)Ph$, a complex analogous to that which we isolated from the platinum reaction. Since nickel σ-cyclopentadienyl derivatives are much less stable than their palladium and platinum counterparts, reductive elimination of PhC_5H_5 from the nickel compound is likely. Reaction of the remaining portion with excess CO would then yield $(Ph_3P)Ni(CO)_3$.

σ-Bonded compounds, as well as π-bonded ionic species, can also be prepared from the reactions between mononuclear complexes L_2PtX_2 and C_5H_5Tl. The nature of the solvent and the neutral ligands determine which course the reactions will take. Orthophenylenebisdiethylarsineplatinum II chloride reacts with cyclopentadienyl thallium, in T.H.F. at room temperature, to produce a remarkably stable σ-bonded complex.

$$[(C_6H_4(AsEt_2)_2]\ PtCl_2 + C_5H_5Tl \longrightarrow C_6H_4(AsEt_2)_2Pt(\sigma\text{-}C_5H_5)Cl + TlCl$$

This is a mustard coloured compound, stable in air and decomposing ca.140°. It is interesting to note that decomposition, plus some salt formation, occurs if chelating phosphines such as $Ph_2PC_2H_4PPh_2$ or $Me_2PC_2H_4PMe_2$

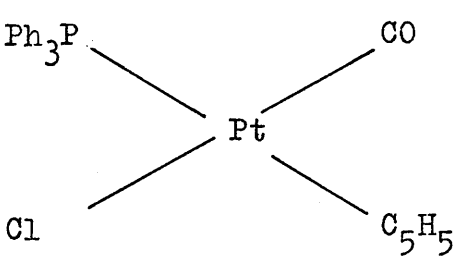
are used as neutral ligands instead of the diarsine.

Cyclopentadienyl thallium also reacts with cis-$(Ph_3P)(CO)PtCl_2$ to produce a σ-bonded complex, $(Ph_3P)(CO)Pt(\sigma\text{-}C_5H_5)Cl$. This yellow-orange solid was rather unstable and decomposed, with loss of CO, during attempted recrystallisation from ethanol.

The varying tendencies of the platinum complexes to produce either the ionic or the σ-bonded cyclopentadienyl derivatives can be rationalised from their stereochemistry and the nature of the ligands. Bis-phosphine organoplatinum halides commonly adopt a trans configuration. Thus, the complex initially formed from C_5H_5Tl and $(Et_3P)_2PtX_2$ or from $(\pi\text{-}C_5H_5)(Et_3P)PtX$ and Et_3P is likely to be trans-$(Et_3P)_2Pt(\sigma\text{-}C_5H_5)X$. The high trans-effect of C_5H_5 will then promote the loss of X^- and hence conversion to $[(\pi\text{-}C_5H_5)(Et_3P)_2Pt]^+X^-$. In the case of the phenyl derivative $(Et_3P)_2Pt(\sigma\text{-}C_5H_5)Ph$, $\sigma \longrightarrow \pi$ conversion of the C_5H_5 ligand is prevented by lack of a suitable leaving group, and the trans stereochemistry of this complex is shown by the fact that the C_5H_5 resonance in the n.m.r. consists of a triplet due to coupling of the ring protons to the two equivalent phosphorus atoms.

The ligands R_3P and CO frequently adopt a mutual cis arrangement at platinum. The chloride ligand in $(Ph_3P)(CO)Pt(\sigma\text{-}C_5H_5)Cl$ is not, therefore, trans to the cyclopentadienyl ring and is not eliminated. The complex $[(C_6H_4(AsEt_2)_2]Pt(\sigma\text{-}C_5H_5)Cl$ is also constrained in the cis position by the chelating ligand, accounting for its stability.

The magnitude of J(P-H) is greater for $(Et_3P)(CO)Pt(C_5H_5)Ph$ and $(Ph_3P)(CO)Pt(C_5H_5)Cl$ (ca.4Hz.) than for $(Et_3P)_2Pt(C_5H_5)Ph$ and $(Et_3P)(Ph_3P)Pt(C_5H_5)Ph$ (ca. 1.2Hz). Since both phosphines are cis to C_5H_5 in the latter compounds (a triplet being observed for the C_5H_5 resonance), the higher coupling constants of the former can then be accounted for by R_3P being trans to C_5H_5. This is consistent with the arguments used to rationalise the formation of $(Ph_3P)(CO)Pt(\sigma\text{-}C_5H_5)Cl$ rather than $[(\pi\text{-}C_5H_5)(Ph_3P)(CO)Pt]^+Cl^-$ and assigns the configuration shown below.



We have shown that the stability of σ-cyclopentadienyl derivatives depends markedly on the nature of

the metal. Thus, in the systems which we have studied it has been possible to both detect and isolate σ-C_5H_5 complexes of platinum, to detect but not isolate several of palladium, but it has not been possible to even detect any of the nickel species.

The products formed in the reactions between the bisphosphine metal halide complexes and C_5H_5Tl also depend on the nature of the metal.

$$(R_3P)_2NiX_2 + C_5H_5Tl \longrightarrow (\pi\text{-}C_5H_5)(R_3P)NiX + R_3P + TlX$$

$$(R_3P)_2MX_2 + C_5H_5Tl \longrightarrow [(\pi\text{-}C_5H_5)(R_3P)_2M]^+X^- + TlX \qquad (M = Pd,Pt)$$

π-Bonded ionic cyclopentadienyls are produced for palladium and platinum and we have suggested above that trans-$(R_3P)_2M(C_5H_5)X$ is an intermediate. It is possible that the nickel reaction follows a similar course.

$$(R_3P)_2NiX_2 + C_5H_5Tl \longrightarrow \text{trans-}(R_3P)_2Ni(\sigma\text{-}C_5H_5)X + TlX$$

$$\downarrow$$

$$[(\pi\text{-}C_5H_5)(R_3P)_2Ni]^+X^-$$

$$\downarrow$$

$$(\pi\text{-}C_5H_5)(R_3P)NiX + R_3P$$

The last stage of the mechanism, conversion of the ionic species to the observed product, $(\pi\text{-}C_5H_5)(R_3P)NiX$, has recently been shown to be plausible by the report of Sato

and co-workers[110] that $[(\pi\text{-}C_5H_5)(Bu_3P)_2Ni]^+Cl^-$ is unstable in solution and readily converts to $(\pi\text{-}C_5H_5)(Bu_3P)NiCl$.

To conclude this discussion, the chemistry of the cyclopentadienyl derivatives of the nickel group appears to be dominated by facile $\sigma \longrightarrow \pi$ interconversions of the C_5H_5 ligand. Such rearrangements have been observed in organometallic compounds of almost all the transition metals and with a large variety of ligands.[111] Our observation may be of importance when one considers the number of catalytic systems in which $\sigma \longrightarrow \pi$ rearrangements of coordinated organic ligands are thought to occur. One such system, the OXO process, involves the addition of hydrogen and carbon monoxide to olefins, to give higher alcohols, using a cobalt-carbonyl catalyst. The important step in this process is thought to involve conversion of a π-olefin complex to a σ-derivative.[111]

$$R\,CH = CHR^1 \;\underset{H\text{-}Co(CO)_3}{\downarrow} \quad \rightleftharpoons \quad RCH_2 - \overset{R^1}{\underset{|}{C}}HCo(CO)_3$$

It is possible that the intrinsic variation in the number of co-ordination sites occupied by C_5H_5 at nickel, palladium and platinum may also be of value in some catalytic processes.

2. Some reactions of the complexes.

(a) $(\pi\text{-}C_5H_5)(R_3P)MX$ (M = Pd,Pt; X = halogen) and C_5H_5Tl

In view of the current interest in fluxional organometallic molecules,[112] we were interested in determining whether the halogen atom in the complexes of the form $(\pi\text{-}C_5H_5)(R_3P)MX$ (M = Pd,Pt) could be replaced by a cyclopentadienyl group to yield a product containing two C_5H_5 ligands each bonded to the metal atom in a different manner. The reactions which we studied are listed below.

(1) $(\pi\text{-}C_5H_5)(Et_3P)PdBr + C_5H_5Tl \longrightarrow (C_5H_5)_2Pd(PEt_3) + TlBr$

(2) $(\pi\text{-}C_5H_5)(Et_3P)PdBr + (C_5H_5)_2Hg \longrightarrow$ no reaction

(3) $(\pi\text{-}C_5H_5)(Ph_3P)PdBr + C_5H_5Tl \longrightarrow$ yellow solid

(4) $(\pi\text{-}C_5H_5)(Et_3P)PtI + C_5H_5Tl \longrightarrow$ red oil

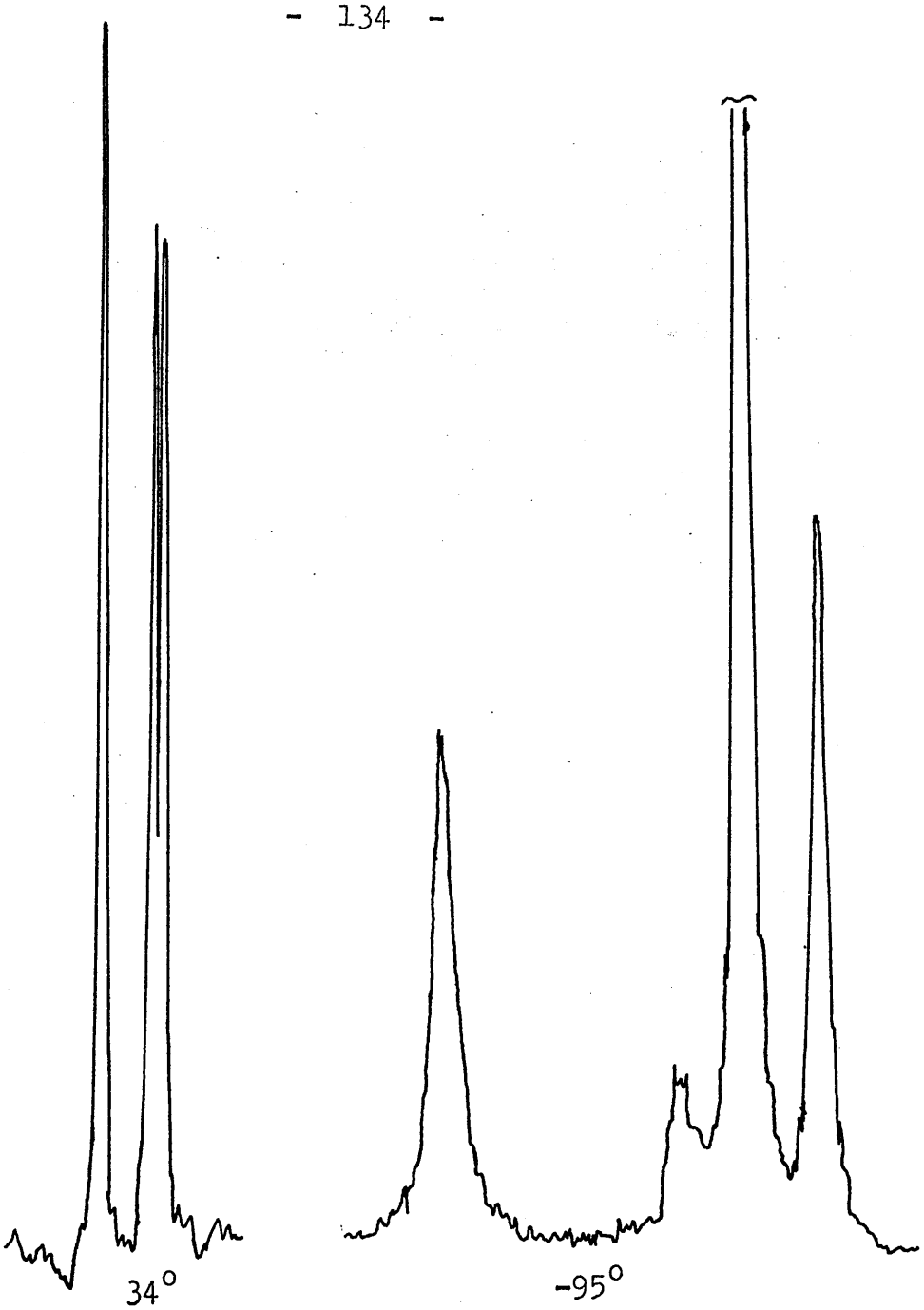
All the reactions were performed in benzene at room temperature. Reactions (3) and (4), after filtering and removal of solvent, yielded a yellow solid and a red gum respectively, neither of which showed any cyclopentadienyl resonances in the ^1H n.m.r. spectrum. Reaction (2) was examined by n.m.r. spectroscopy. No reaction was observed in C_6D_6 within 24 hours after which time slow decomposition ensued, possibly due to decomposition of the unreacted organomercurial.

Reaction (1) required 3 hours to reach completion, as shown by n.m.r. spectroscopy, and after work-up in the

usual manner gave a green-brown oil. This material proved very difficult to handle, since it decomposes above 40° and is moderately air sensitive. The problems of obtaining and keeping pure samples of this compound added to the difficulty of determining its constitution.

The physical techniques of n.m.r., i.r. and mass spectroscopy were employed in the structural investigation. The mass spectrum of the complex showed a molecular ion at 354 corresponding to $(C_5H_5)_2(Et_3P)Pd^+$ (M = 354).

At room temperature the C_5H_5 region of the ^1H n.m.r. spectrum of $(C_5H_5)_2Pd(PEt_3)$ in d^8- toluene included a singlet at τ 4.3 and a doublet at τ 4.55(J(P-H)2Hz) . On cooling the solution to -95°, the doublet remained invariant, but the singlet was replaced by three peaks at τ 3.67, τ 4.39 and τ 4.77, integrating in the ratio 2:1:2. Figure 9 shows the spectra observed at (1) 34° and (2) -95°. The fact that the doublet at τ 4.55 is unchanged with temperature indicates that the resonance is associated with a π-bonded cyclopentadienyl ring. If we consider the complex to be formed from a neutral palladium atom and neutral ligands, then the neutral Pd atom requires a total of 8 electrons from the surrounding ligands in order to attain the rare gas configuration. In $(C_5H_5)_2Pd(PEt_3)$,



Cyclopentadienyl region of $(C_5H_5)_2Pd(PEt_3)$

FIGURE 9.

the palladium atom receives 2 electrons from the tertiary phosphine and 5 electrons from the π-C_5H_5 ring. The remaining electron is then accounted for if the other C_5H_5 ring is σ-bonded. The resulting formulation (π-C_5H_5)(σ-C_5H_5)Pd(PEt_3) can explain the structure of the n.m.r. spectrum. At room temperature, the σ-C_5H_5 ring is fluxional giving rise to the single resonance at τ 4.3, and the doublet at τ 4.55 is due to coupling of the equivalent π-C_5H_5 protons with phosphorus. At -95° the motion of the fluxional cyclopentadienyl ring has been arrested, allowing the non-equivalence of the protons to be established.

Low temperature n.m.r. spectra of fluxional σ-C_5H_5 species normally exhibit[8] two sets of peaks in the 3-4τ region, associated with the 4 olefinic protons and a peak at ca.τ 6 due to the proton on the carbon directly bonded to the metal. The peaks observed for our compound, at τ 3.67 and τ 4.77 for the olefinic protons and τ 4.39 for the unique proton, do not, therefore, appear in the normal positions for a σ-C_5H_5 ring.

The other possibility is that the complex should be formulated as (h^5-C_5H_5)(h^3-C_5H_5)Pd(PEt_3), i.e. the fluxional ring is a π-allylic cyclopentadienyl ring. The intensity and position of the peaks in the low

temperature spectrum are in accord with this formulation. However, the palladium atom would then have 20 electrons in the outer bonding orbitals making the complex extremely unstable and possibly paramagnetic.

Taking these factors into consideration, the most likely method of bonding appears to be (π-C_5H_5)(σ-C_5H_5)-$Pd(PEt_3)$, although the anomalous position of the peaks associated with the σ-C_5H_5 protons is not understood.

The i.r. spectrum of the complex showed 18 peaks associated with vibrations of the C_5H_5 ligands (see table 18

If we take the vibrations at 3079 and/or 3060, 1398, 1102, 825 and 765cm^{-1} as being associated with the π-bonded cyclopentadienyl ring, the remaining 12 or 13 peaks are derived from either σ- or π-allylic C_5H_5 species. The position and intensity of these peaks are similar to those observed for σ-cyclopentadienyl platinum derivatives, and this provides further evidence for the formulation, (π-C_5H_5)(σ-C_5H_5)$Pd(PEt_3)$. We now have sufficient information to compare the effect of C_5H_5Tl on analogous π-cyclopentadienyl derivatives of the nickel group.

(π-C_5H_5)$(Et_3P)NiCl$ + C_5H_5Tl $\longrightarrow$ (π-C_5H_5)$_2Ni$ + Et_3P + TlCl

(π-C_5H_5)$(Et_3P)PdBr$ + C_5H_5Tl $\longrightarrow$ (π-C_5H_5)(σ-C_5H_5)$Pd(PEt_3)$ + TlBr

(π-C_5H_5)$(Et_3P)PtI$ + C_5H_5Tl $\longrightarrow$ decomposition

It has been suggested in section 1 of this chapter that the nickel reaction produces (π-C_5H_5)(σ-C_5H_5)Ni-(PEt_3) as an unstable intermediate. This is substantiated by the isolation of the derivative (π-C_5H_5)(σ-C_5H_5)Pd(PEt_3) from the palladium reaction. It is surprising, however, that no such species is formed from (π-C_5H_5)(Et_3P)PtI and C_5H_5Tl since we have shown that platinum σ-cyclopentadienyl complexes are much more stable than their palladium analogues. It may be that addition of the second C_5H_5 group to (π-C_5H_5)(Et_3P)-PtI is sufficient to cause $\pi \longrightarrow \sigma$ conversion of the other group to yield (σ-C_5H_5)$_2$Pt(PEt_3). Reductive elimination of $C_{10}H_{10}$ could then occur.

(b) (π-C_5H_5)(R_3P)MX (M = Pd,Pt) and $N_2H_4H_2O$

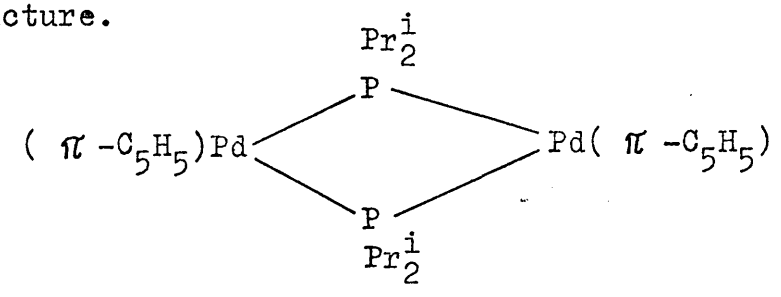
The stability of square planar metal-hydride complexes of the nickel group increases in the order Ni < Pd < Pt. Thus, although hydrides of platinum are well established,[25] it is only recently that the first nickel hydride was reported.[113] Yamazaki and co-workers attempted to prepare a nickel hydride derivative by reacting (π-C_5H_5)(Ph_3P)NiCl with $LiAlH_4$ but observed the following reaction instead.[71]

(π-C_5H_5)(Ph_3P)NiCl + $LiAlH_4$ $\longrightarrow$ [(π-C_5H_5)$NiPPh_2$]$_2$

We wished to determine whether, by changing the metal atom from Ni to Pd or Pt, we could isolate a stable cyclopentadienyl metal hydride derivative. A milder reducing agent was also employed. The complexes (π-C_5H_5)(R_3P)MX (M = Pd,Pt) were, therefore, reacted with aqueous hydrazine in methanol.

Solutions of the green palladium derivatives (π-C_5H_5)(R_3P)PdBr (R = Et, ^iPr) immediately changed to red on addition of hydrazine and evolution of gas was observed. Dark red needle-like crystals were obtained from the work-up in both cases. The complexes are rather unstable and are best stored at -20° under nitrogen.

Infrared and n.m.r. spectroscopy showed that complexes containing the palladium-hydride bond were not present. The n.m.r. spectrum, in C_6D_6, of the complex produced by reacting (π-C_5H_5)(Pr_3^iP)PdBr with $N_2H_4 \cdot H_2O$ showed a triplet in the C_5H_5 region centred at τ 4.56 (J(P-H)2.1Hz). On the basis of this observation, plus elemental analysis figures and the analogous nickel reaction, it is suggested that the product has the structure.



The n.m.r. spectrum of the product from (π-C_5H_5)-(Et_3P)PdBr and $N_2H_4 \cdot H_2O$ showed two triplets centred at τ 4.38 (J(P-H)2.3Hz) and τ 4.54 (J(P-H)2.3Hz) in the intensity ratio of 4:1. On the basis of previous considerations it seems reasonable to assign the formula $[(\pi\text{-}C_5H_5)PdPEt_2]_2$ to this complex. The appearance of two triplets in the spectrum is puzzling, however, since it is not possible to envisage more than one isomer with the above structure. The elemental analysis figures were approximately 1% out in both C and H so the explanation as to the structure of the spectrum may be that the smaller triplet is associated with an impurity.

The reaction between the platinum complex, (π-C_5H_5)(Et_3P)PtI, and hydrazine produced a yellow solid which showed no cyclopentadienyl resonances in the n.m.r. spectrum. Thus, we again have the situation of the platinum reaction leading to decomposition, whereas the nickel and palladium reactions form π-cyclopentadienyl products. It is probable that at some stage of the platinum reaction a σ-C_5H_5 species is produced, allowing reductive elimination to occur.

3. $(C_{20}H_{20})Pt_2$

The green, diamagnetic complex, $(C_{20}H_{20})Pt_2$, was first reported by Fischer and Schuster-Woldan.[93] They prepared

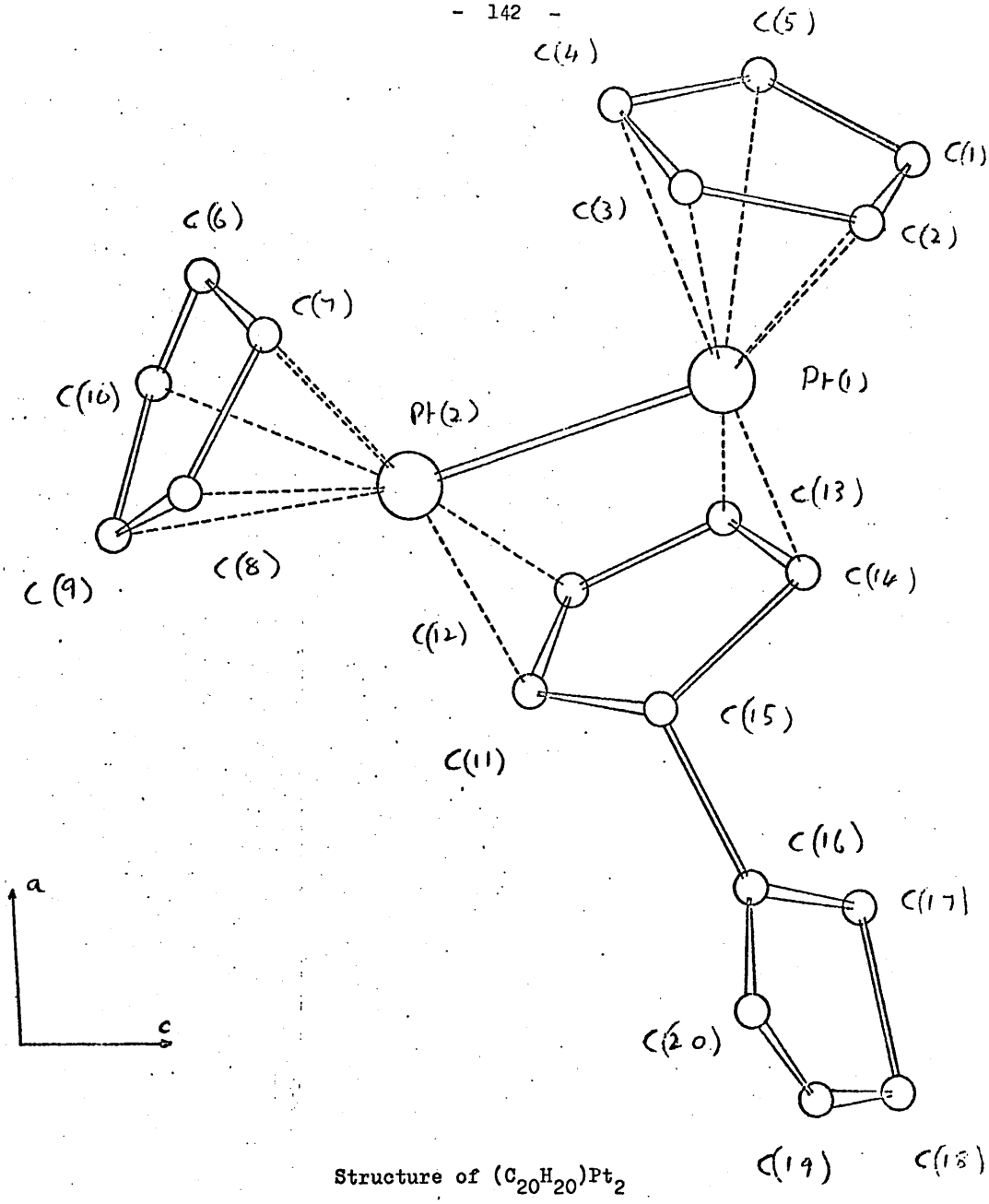
the compound in 3% yield by treating 1 equivalent of $PtCl_2$ with 3 equivalents of C_5H_5Na in hexane for 2 days. We found that the same complex could be prepared in 30 minutes, again in small yield, by using T.H.F. rather than hexane as the solvent. The reaction was not clean and a large amount of platinum metal was produced. In addition to the cyclopentadienyl-platinum derivative, we also isolated an off-white crystalline compound. The mass spectrum of the latter species showed that its constitution is purely organic, and it appears to be a mixture of polymeric cyclopentadienyl chloride derivatives, e.g. $C_{20}H_{23}Cl$ was detected, M = 298.

The stoichiometry of the platinum-containing product, $(C_{20}H_{20})Pt_2$, was derived[93] from the mass spectrum M(mass spectrum) = 650 ; $C_{20}H_{20}Pt_2$[195] requires M = 650 . The n.m.r. spectrum was superficially similar to that of $[(\pi\text{-}C_5H_5)Pt(CO)]_2$, a complex which contains a platinum-platinum bond, and on these grounds the complex was assigned[93] the structure $(C_5H_5)_4Pt_2$ with a Pt-Pt bond and π-and σ-bonded cyclopentadienyl rings in rapid, valence-tautomeric equilibria.

We had reason to question this assignment on two counts. Firstly, such a structure would place a formal valency of three on each platinum atom making the

diamagnetism of the complex difficult to explain. Secondly, we did not observe any change in the n.m.r. spectrum of a toluene-d^8 solution of the complex on cooling to -95°C. Cotton has shown[114] (see n.m.r. section), for a complex in which π - and σ -bonded C_5H_5 rings are exchanging structural roles (as in $Ti(C_5H_5)_4$ for example), that cooling the solution leads to the appearance of peaks typical of both π - and σ -bonded rings.

A crystal structural analysis of the complex was, therefore, undertaken by Drs. K.K. Cheung, K. Forrest and M. Mercer of this department. Crystals of $(C_{20}H_{20})Pt_2$ were prepared for X-ray study by the method previously described.[93] The crystals are monoclinic, space group $P2_{1/c}$, with a = 16.43, b = 5.64, c = 17.11 Å, β = 92.7°, Z = 4, D_m = 2.71 g cm^{-3}, D_c = 2.728 g cm^{-3}. For the X-ray data collection, CuKα radiation and equi-inclination Weissenberg methods were used with a small crystal sealed in a capillary tube rotating about b. The structure was determined by the heavy atom method. Based on 1332 independent reflections, the structure was refined by least-squares, and R = 14.0% at present. The arrangement of the atoms in one molecule projected down the b-axis is shown in figure 10 and the Pt-C distances in the π -bonded systems are listed below. The e.s.d.



Structure of $(C_{20}H_{20})Pt_2$

FIGURE 10.

Pt-C distances in the π-bonded systems

Pt(1) - C(1)	2.33Å	Pt(2) - C(6)	2.36Å
Pt(1) - C(2)	2.36	Pt(2) - C(7)	2.09
Pt(1) - C(3)	2.24	Pt(2) - C(8)	2.33
Pt(1) - C(4)	2.21	Pt(2) - C(9)	2.39
Pt(1) - C(5)	2.32	Pt(2) - C(10)	2.22
Pt(1) - C(13)	2.03	Pt(2) - C(11)	2.00
Pt(1) - C(14)	2.03	Pt(2) - C(12)	2.12

of the Pt-Pt bond is 0.004Å and those involving carbon atoms are 0.08 - 0.09Å at this stage.

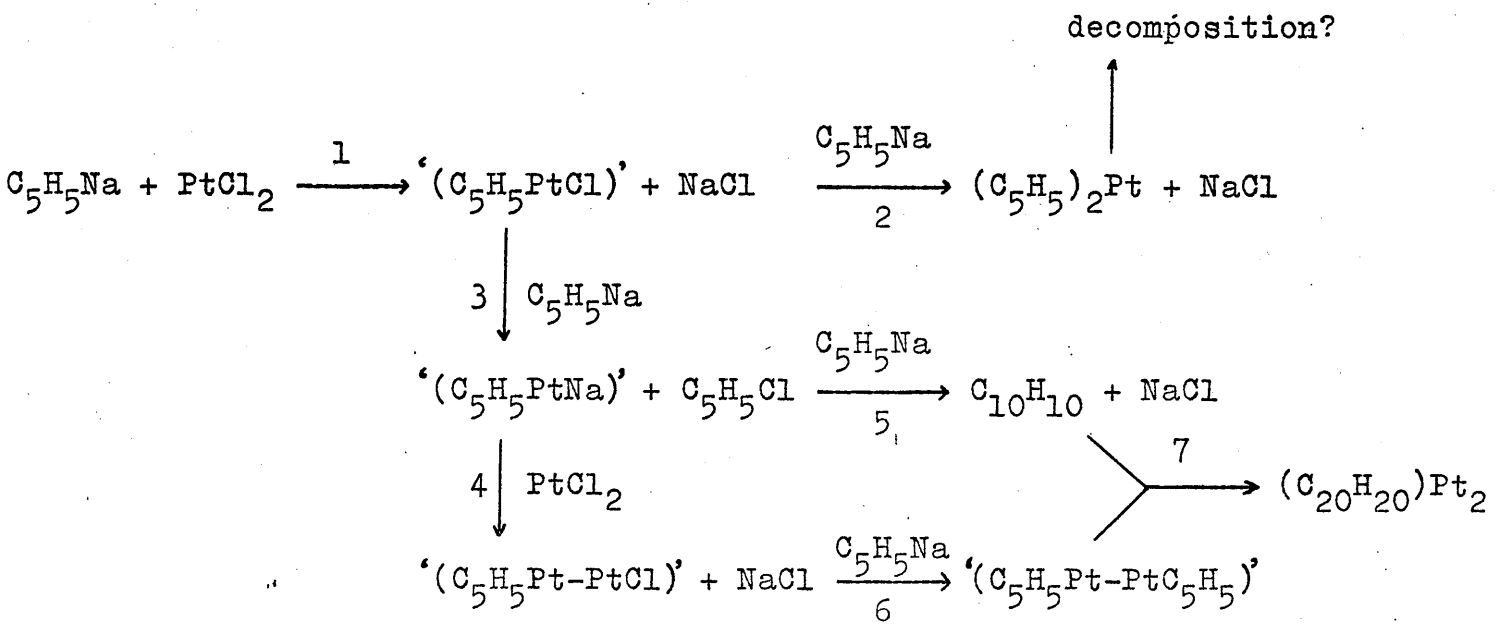
The complex contains a platinum-platinum bond, with a π-cyclopentadienyl ring bound to each metal atom. The Pt-Pt distance is 2.581Å, slightly less than the value of 2.65Å obtained for the single covalent Pt-Pt bond in $Pt_2S(CO)(PPh_3)_3$, the only compound containing a Pt-Pt bond previously examined.[115] The average distance of each platinum atom from the carbon atoms of their π-cyclopentadienyl rings is ca.2.3Å. The corresponding distance in (π-C_5H_5)$PtMe_3$, the only other cyclopentadienylplatinum complex of known structure,[96] is 2.2Å.

The most interesting feature of the structure is the presence of the hitherto unsuspected 5-(5'-cyclopentadienyl)-cyclopentadiene unit bridging the two metal atoms. Each platinum atom bonds to one of the olefinic links of one of the C_5 rings, and the Pt-C distances are ca.205Å, comparable to those in Zeises salt and related compounds. The second ring of the $C_{10}H_{10}$ group is directed away from the platinum atoms and is uncomplexed. The only comparable structures are those reported for the dimers $Rh_2C_{20}H_{20}$ and $Ir_2C_{20}H_{20}$.[116] Here, two π-cyclopentadienylmetal units are believed to be bridged by 5-(5'-cyclopentadienyl)-cyclopentadiene, but no metal-metal bonds are

present and all the olefinic links are coordinated to the metals.

In the light of this structural investigation, it is necessary to revise the previous assignment of the ^{1}H n.m.r. spectrum of $(C_{20}H_{20})Pt_2$. The resonance associated with the π-C_5H_5 rings of the complex is centred at τ 4.37 (in C_6D_6). The existence of the platinum-platinum bond enables the protons of each π-bonded ring to couple not only to the platinum atom to which the ring is directly bound (J ($Pt^{195}H$)15Hz) but also to couple to the other metal atom (J ($Pt^{195}H$)9.5Hz). In this respect, the spectrum resembles that of $[(\pi\text{-}C_5H_5)Pt(CO)]_2$. The spectrum also shows broad peaks, of much lower intensity than the main resonance, at ca. τ 3.5, 4.14, 5.39, 5.95, 6.90, 7.03 and 7.38. These peaks occupy the same area as the resonance at τ 4.37, and must be attributed to the protons of the $C_{10}H_{10}$ bridging ligand.

A speculative mechanism for the formation of this novel compound is outlined on next page.



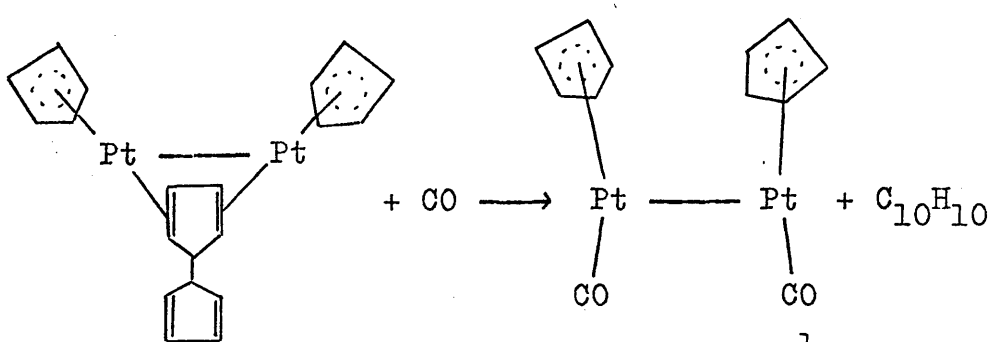
Halogen-metal exchange at stage (3) can lead to formation of '(C_5H_5PtNa)' which could then react with $PtCl_2$ to form the platinum-platinum bond. The cyclopentadienyl chloride produced at stage (3), on treatment with C_5H_5Na may yield $C_{10}H_{10}$. At stage (7) this ligand can react with the Pt-Pt bonded intermediate '$(C_5H_5Pt-PtC_5H_5)$' to form

the observed product, $(C_{20}H_{20})Pt_2$. Reaction of C_5H_5Cl with $C_{10}H_{10}$ may also occur, leading to formation of purely organic cyclopentadienyl chloride derivatives.

Reaction of $(C_{20}H_{20})Pt_2$ with neutral ligands.

The fact that the neutral ligand 5-(5^1-cyclopentadienyl)cyclopentadiene bridges the platinum-platinum bond in $(C_{20}H_{20})Pt_2$ led us to believe that it might be possible to replace this ligand with other neutral species and thus form series of derivatives containing the Pt-Pt bond.

Treatment of a solution of $(C_{20}H_{20})Pt_2$ in benzene with carbon monoxide led to the formation of a red compound, which was characterised by i.r., n.m.r. and mass spectroscopy as the known complex $[(\pi\text{-}C_5H_5)Pt(CO)]_2$. This species contains a metal-metal bond with terminal $\pi\text{-}C_5H_5$ and carbonyl ligands, so that the reaction proceeds as we had anticipated.



Tertiary phosphines can also replace 5-(5^1-cyclopentadienyl)cyclopentadiene from $(C_{20}H_{20})Pt_2$, since

resonances associated with the free $C_{10}H_{10}$ ligand were observed in the n.m.r. spectrum on addition of R_3P (R = Ph,Bu) to a solution of the platinum complex in C_6D_6. Total decomposition of the reaction mixture ensued within 15 minutes, however, with the result that no products could be isolated. In view of our earlier observations on the reactions between tertiary phosphines and π-cyclopentadienyl platinum complexes, it is probable that $\pi \longrightarrow \sigma$ conversion of co-ordinated C_5H_5 groups is being effected in this case also, with resultant decomposition of the unstable σ-bonded species.

No reaction was observed when cis-cyclooctadiene was added to a solution of $(C_{20}H_{20})Pt_2$ in benzene.

4. Spectroscopic examination of Complexes.

(a) Nuclear Magnetic Resonance

Introduction.

A cyclopentadienyl ring π-bonded to a metal atom usually exhibits a single resonance in the ^1H n.m.r. spectrum near $\tau = 5$. The protons of such a ring appear, in general, to be magnetically equivalent, even when other groups around the metal tend to reduce the symmetry. Rapid rotation about the metal to ring axis is probably responsible for averaging out possible anisotropies in the shielding of the ring protons.

The ring proton resonance can be split into multiplets by spin-spin coupling either with isotopes of the metal to which it is bonded (if $I \neq 0$) or with other nuclei which are bonded to the metal, such as hydrogen or phosphorus. The splittings in the former case range from 1Hz, as in (π-C_5H_5)RhC_5H_6[117] (J (Rh^{103}- C_5H_5)1.0Hz) up to 18.5Hz for (π-C_5H_5)Pt(CO)I[118] (J (Pt^{195}-H) 18.5Hz). The splitting of the ring proton resonance by other nuclei bonded to the metal is always of a smaller order, e.g. (π-C_5H_5)$_2WH_2$[119] (J (C_5H_5-H) 0.75Hz), cis-[(π-C_5H_5)Fe-(CO)PMe_2]$_2$[120] (J (P-C_5H_5)1.0Hz) and [(π-C_5H_5)$NiPPh_2$]$_2$[121] (J (P-C_5H_5)0.6Hz). In fact, the cyclopentadienyl nickel complex [(π-C_5H_5)$NiPPh_2$]$_2$ is the only nickel derivative containing a π-bonded C_5H_5 ring and a phosphine ligand to exhibit this type of phosphorus-hydrogen coupling. Thus, the cyclopentadienyl resonance for compounds of the form (π-C_5H_5)(R_3P)NiL (L = halogen, organic group) is always a singlet.[106] In contrast, the values of J(P-C_5H_5) for the isoelectronic complexes (π-C_5H_5)(R_3P)(CO)M[122] (M = Rh, Ir) are in the region of 2Hz.

The ^1H n.m.r. spectrum of a complex containing a cyclopentadienyl ring σ-bonded to the metal should theoretically consist of groups of resonances for the

C_5H_5 protons in the relative intensity ratio 1:2:2. In practice, such a spectrum is seldom observed at room temperature for a σ-cyclopentadienyl metal derivative since the metal-carbon bond rapidly shifts between the five possible positions making all the protons equivalent. As described previously, solutions of cyclopentadienyl mercury derivatives have to be cooled to ca.-120° in order to observe the instantaneous structure.

Cotton and co-workers have examined a wide range of metal complexes containing more than one cyclopentadienyl ring (see for example refs. 8, 114, 123) each ring being bonded to the metal atom in a different manner. The first molecule containing both a σ-C_5H_5 and a π-C_5H_5 group attached to the same metal atom to be studied as a function of temperature by n.m.r. spectroscopy was (π-C_5H_5)$Fe(CO)_2$ (σ-C_5H_5).[8] It was shown (see figure 2) that the σ-C_5H_5 ring is fluxional and the available evidence favours 1, 2 shifts as the predominant rearrangement pathway. No indication of structural interchange of the two rings has been observed even up to temperatures of ca.125°. Recently, however, facile interchange of σ-C_5H_5 and π-C_5H_5 rings has been shown by a variable temperature n.m.r. study of

$(\pi\text{-}C_5H_5)_2(\sigma\text{-}C_5H_5)_2Ti$[114].

Two resonance lines are observed at -30°, one due to the fluxional σ-C_5H_5 rings and the other to the π-C_5H_5 rings. As the temperature rises, these two lines collapse and merge, proving that ring interchange occurs. This interchange is attributed to the formal 16-electron configuration, which means that the metal atom possesses an empty orbital. This orbital may be employed in bonding two rings, which are initially π-C_5H_5 and σ-C_5H_5, in an equivalent fashion, thus affording a suitable, low-energy transition state.

The two known limiting cases of metal-cyclopentadienyl bonding, viz. the $(\pi\text{-}C_5H_5)M$ case which is designated pentahapto (h^5) by Cotton,[124] and the $(\sigma\text{-}C_5H_5)M$ case which in the same notational system is called monohapto (h^1), have been widely discussed in the literature. There is also a seemingly logical possibility of the intermediate case existing, with the C_5H_5 ring behaving as a π-allylic type of ligand (a trihapto ligand, h^3). As yet, no certain example of this situation has been found. The most likely cases, though not proved, are provided by $(C_5H_5)_2Mo(NO)I$ and $(C_5H_5)_2Mo(NO)CH_3$, both described by King.[125] A neutral molybdenum atom requires a total of

12 electrons from the surrounding ligands to conform to the 18 electron rule. In $(C_5H_5)_2Mo(NO)R$ (R = I,CH_3), the Mo atom receives one electron from R and three electrons from the nitrosyl ligand, leaving a total of 8 electrons to be received from the two C_5H_5 ligands. If one of the cyclopentadienyl groups is π-bonded, the other C_5H_5 ring should then contribute 3 electrons and behave as a π-allylic ligand. Only 1 n.m.r. signal for the cyclopentadienyl protons is observed even as low as -55°, however, and King has suggested that (a) the h^3 C_5H_5 ring is fluxional and (b) rapid interchange of the rings is occurring.

Parameters of previously reported cyclopentadienyls of Pd and Pt.

All the cyclopentadienyl complexes of palladium and platinum so far reported have the C_5H_5 ring π-bonded to the metal atom, with the exception of the cis- and trans-isomers of $(Me_2S)_2Pt(C_5H_5)_2$. The ^1H n.m.r. parameters for the compounds are recorded in table 12 for palladium and table 13 for platinum. The palladium derivatives show a singlet for the cyclopentadienyl protons since all five are equivalent and there are no other isotopes present which can cause spin-spin splitting. In general, the

TABLE 12

Cyclopentadienylpalladium complexes.

Compound	Solvent	Chemical Shift (τ) of C_5H_5	Ref.
$(\pi\text{-}C_5H_5)PdNO$	C_6H_6	4.75	84
$(\pi\text{-}C_5H_5)PdC_3H_5$	C_6H_6	4.14	85,86
$(\pi\text{-}C_5H_5)PdC_6H_9$	C_6H_6	4.08	86
	CCl_4	4.35	
$(\pi\text{-}C_5H_5)PdC_{10}H_{12}OCH_3$	CS_2	4.47	87
	$CDCl_3$	4.37	88
$(\pi\text{-}C_5H_5)PdC_4Ph_4H_2OH$	$CDCl_3$	4.44	89
$(\pi\text{-}C_5H_5)PdC_4Ph_4H_2OMe$	$CDCl_3$	4.55	89
$(\pi\text{-}C_5H_5)PdC_4Ph_4H_2OEt$	$CDCl_3$	4.55	89
$[(\pi\text{-}C_5H_5)PdC_8H_{12}]^+BF_4^-$	$CDCl_3$	3.75	90
$[(\pi\text{-}C_5H_5)PdC_4Ph_4]^+Br^-$	$CDCl_3$	3.66	89
$[(\pi\text{-}C_5H_5)PdC_4Ph_4]^+FeBr_4^-$	paramagnetic		89
$[(\pi\text{-}C_5H_5)PdC_8H_{12}]^+FeBr_4^-$	paramagnetic		89

TABLE 13

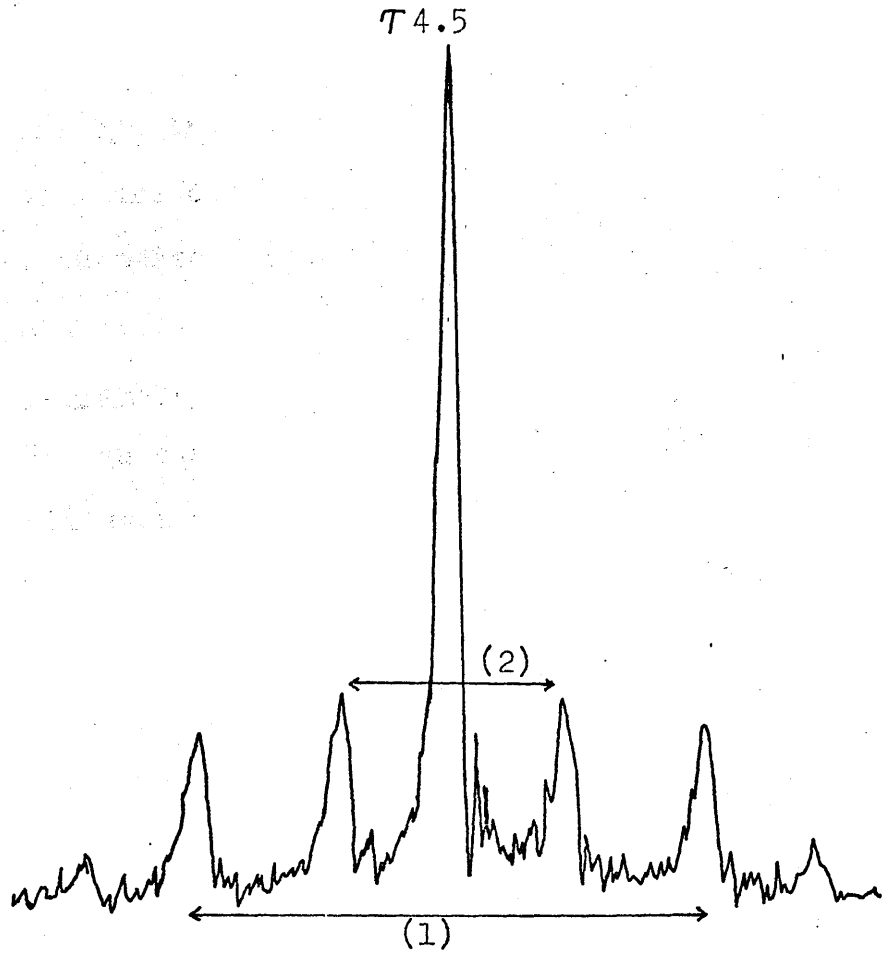
Cyclopentadienylplatinum complexes.

Compound	Solvent	Chemical shift (τ)	$J_{(Pt-H)}$ Hz	Ref.
$(\pi\text{-}C_5H_5)PtNO$	C_6H_6	4.93	17.0	91
$(\pi\text{-}C_5H_5)PtC_3H_5$	C_6H_6	4.25	10.5	86
$(\pi\text{-}C_5H_5)PtC_8H_{12}OMe$	$CDCl_3$	4.34	13.5	88
$(\pi\text{-}C_5H_5)PtC_{10}H_{12}OMe$	$CDCl_3$	4.42	13.5	88
$(\pi\text{-}C_5H_5)Pt(CO)I$	C_6H_6	4.87	18.5	118
$[(\pi\text{-}C_5H_5)Pt(CO)]_2$	C_6H_6	4.5	13.7,6	118
$(\pi\text{-}C_5H_5)PtMe_3$		4.39	5.8	94
$[(\pi\text{-}C_5H_5)PtC_8H_{12}]^+BF_4^-$	$CDCl_3$	3.74	17.0	90
cis-$(Me_2S)_2Pt(\sigma\text{-}C_5H_5)_2$	$CDCl_3$	3.92		95
trans-$(Me_2S)_2Pt(\sigma\text{-}C_5H_5)_2$	$CDCl_3$	3.72	36.5	95

resonance occurs at ca. τ 4.5 with the exception of the salts $[(\pi\text{-}C_5H_5)PdC_8H_{12}]^+BF_4^-$ and $[(\pi\text{-}C_5H_5)PdC_4Ph_4]^+Br^-$ which show $\tau(C_5H_5)$ at 3.75 and 3.66 respectively. In these cases charge is presumably drained from the cyclopentadienyl ring causing deshielding of the ring protons.

The π-cyclopentadienyl platinum derivatives exhibit coupling of the ring protons to Pt^{195}, which is 33% abundant, and values of $J(Pt^{195}\text{-}H)$ range from 5.8Hz for the platinum IV complex $(\pi\text{-}C_5H_5)PtMe_3$ to 18.5Hz for $(\pi\text{-}C_5H_5)Pt(CO)I$. The most complicated spectrum is obtained for $[(\pi\text{-}C_5H_5)PtCO]_2$ (see figure 11). This complex contains a Pt-Pt bond and coupling of the C_5H_5 protons to both platinum atoms is observed, $J(Pt^{195}(1)\text{-}H)$ being 13.7Hz and $J(Pt^{195}(2)\text{-}H)$ 6Hz.

The cyclopentadienyl rings of the unstable cis- and trans-isomers of $(Me_2S)_2Pt(C_5H_5)_2$ are apparently fluxional, since all ten protons of each isomer are equivalent at room temperature. The resonances are centred at τ 3.92 for the cis-isomer and τ 3.72 for the trans, markedly lower than the values observed for any of the π-bonded derivatives. It is also worthy of note that the value of 36.5Hz for $J(Pt^{195}\text{-}H)$ of the trans-isomer is appreciably higher than the platinum-hydrogen coupling constants observed for the $\pi\text{-}C_5H_5$ complexes.



(1) J(Pt(1)-H) 13.7Hz

(2) J(Pt(2)-H) 6 Hz

N.m.r. spectrum of $[(\pi\text{-}C_5H_5)PtCO]_2$

FIGURE 11.

The spectra observed for the derivatives prepared in this work are described in the following sections. The n.m.r. parameters (and i.r.) proved extremely useful in assigning structures.

π-Cyclopentadienyl complexes.

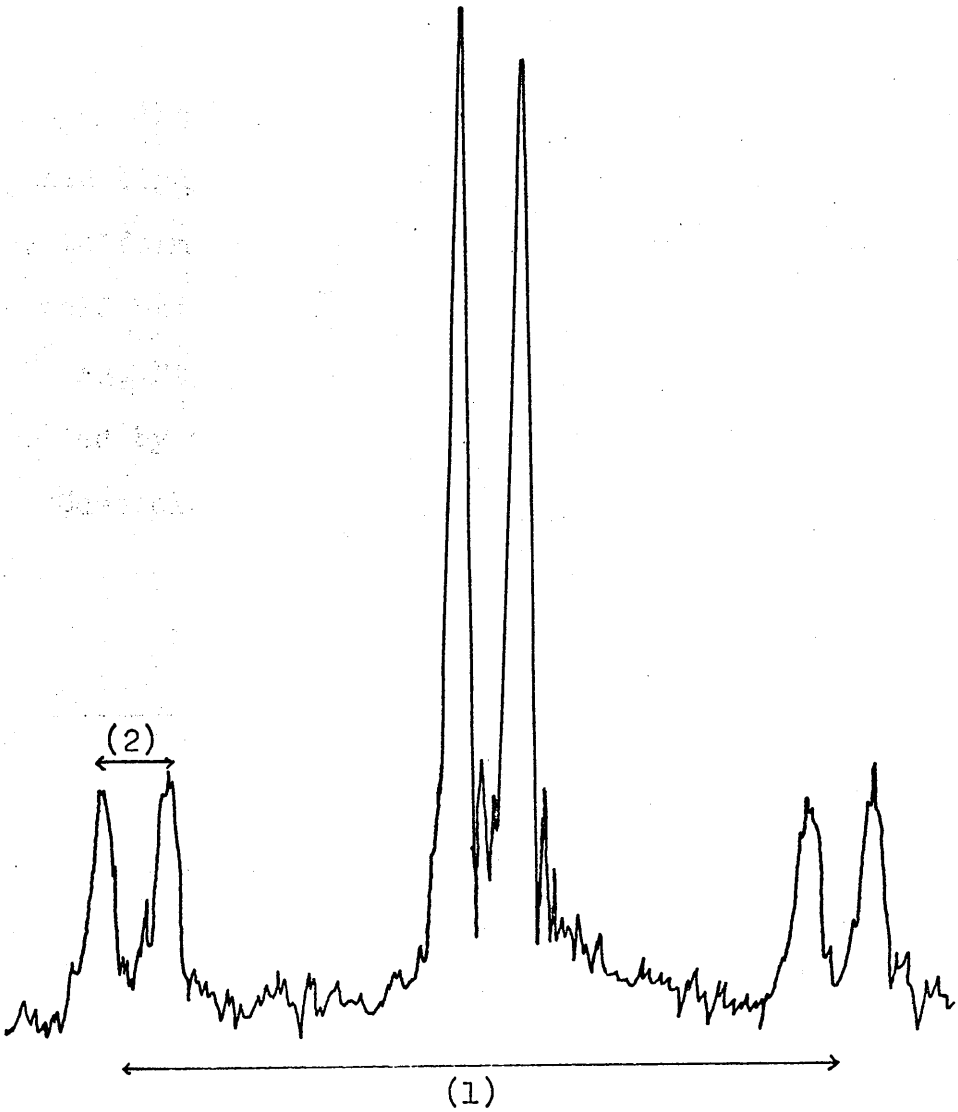
Proton n.m.r. parameters for the π-cyclopentadienyl derivatives are listed in table 14. The main difference between the palladium and platinum complexes and analogous nickel derivatives is that coupling of the ring protons to phosphorus (J(P-H)ca.2Hz) is observed for the heavier metals. As noted previously, coupling of this nature is very rarely observed in nickel complexes and weaker nickel-phosphorus bonds may explain this. The cyclopentadienyl signals in $(\pi\text{-}C_5H_5)(R_3P)MX$ (M = Pd,Pt) are symmetrical doublets and in $[(\pi\text{-}C_5H_5)(R_3P)_2M]$ X they are 1:2:1 triplets. The spectra of the platinum derivatives is further complicated by coupling to Pt^{195}, and $J(Pt^{195}\text{-}H)$ ranges from 11Hz in the salts $[(\pi\text{-}C_5H_5)(Et_3P)_2Pt]$ X to 19Hz for $(\pi\text{-}C_5H_5)(Et_3P)PtI$. The spectrum of the latter complex in the cyclopentadienyl region is shown in figure 12.

The chemical shifts of the ring protons in our compounds fall in general between τ4.1 and τ4.6, which

TABLE 14.

N.m.r. parameters of π-cyclopentadienyl complexes.

Complex	Solvent	$\tau(C_5H_5)$	$J_{(P-H)}$ Hz	$J_{(^{195}Pt-H)}$ Hz
$(Et_3P)(C_5H_5)PdCl$	C_6D_6	4.48	2.5	
$(Et_3P)(C_5H_5)PdBr$	C_6D_6	4.47	2.5	
$(Et_3P)(C_5H_5)PdI$	C_6D_6	4.39	2.5	
$(Pr^i_3P)(C_5H_5)PdBr$	C_6D_6	4.51	2.5	
$(Ph_3P)(C_5H_5)PdBr$	C_6D_6	4.58	2.5	
$(Et_3P)(C_5H_5)PdPh$	C_6D_6	4.25	2.0	
$[(Et_3P)_2(C_5H_5)Pd]Br$	$CDCl_3$	4.17	2.0	
$[C_5H_5Pd(PEt_2)]_2$	C_6D_6	4.38	2.3	
		4.54	2.3	
$[C_5H_5Pd(PPr^i_2)]_2$	C_6D_6	4.56	2.1	
$(C_5H_5)_2PdPEt_3$	C_7D_8	4.30		
		4.55	2.0	
$(Et_3P)(C_5H_5)PtI$	C_6D_6	4.47	2.0	19.0
$(Et_3P)(C_5H_5)PtPh$	C_6D_6	4.25	1.5	12.0
$(Et_3P)(C_5H_5)Pt(o\text{-tolyl})$	C_6D_6	4.30	1.5	11.5
$(Bu^n_3P)(C_5H_5)Pt(COPh)$	C_6D_6	4.30	1.5	13.0
$[(Et_3P)_2(C_5H_5)Pt]Cl$	$CDCl_3$	4.13	1.2	11.0
$[(Et_3P)_2(C_5H_5)Pt]ClO_4$	$CDCl_3$	4.20	1.2	11.0



(1) J(Pt-H) 19.0Hz

(2) J(P-H) 2.0Hz

Cyclopentadienyl region of $(\pi\text{-}C_5H_5)(Et_3P)PtI$ centred at τ 4.47

FIGURE 12.

is lower than those of their nickel analogues.[106] Replacement of the halogen substituent in $(\pi\text{-}C_5H_5)(R_3P)MX$ by an organic ligand forming $(\pi\text{-}C_5H_5)(R_3P)MR^1$, or by a phosphine, to form the salt $\left[(\pi\text{-}C_5H_5)(R_3P)_2M\right]X$, results in a downfield shift of the cyclopentadienyl proton resonance (M = Ni,[106] Pd, Pt). For the platinum complexes, the shift is accompanied by a lowering of J(Pt-H) from ca.19Hz to ca.12Hz. Some electron density in the $(\pi\text{-}C_5H_5)M$ region may be transferred to the new ligand, reducing the metal-ring interaction and thereby the coupling mechanism.

<u>σ-Cyclopentadienyl complexes</u>.

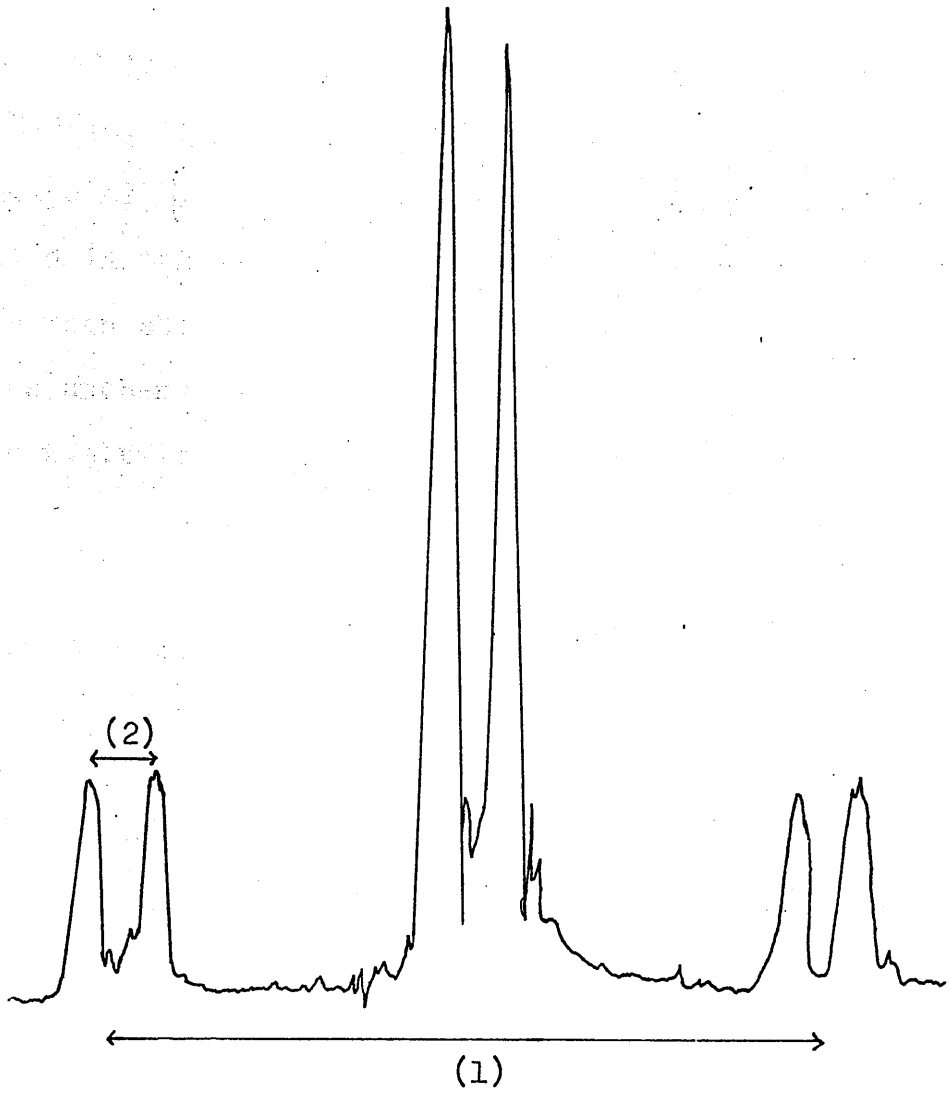
Table 15 gives the n.m.r. parameters for the σ-cyclopentadienyls prepared in this work. The cyclopentadienyl region of the spectrum of $(Ph_3P)(CO)Pt(C_5H_5)Cl$ is shown in figure 13, and this pattern is typical of all the platinum complexes, with the exception of $\left[(C_6H_4)(AsEt_2)_2\right]Pt(C_5H_5)Cl$ where no coupling to phosphorus is possible. The ring protons appear to be equivalent so the molecules must be fluxional, in common with other σ-bonded metal cyclopentadienyls.[112]

A notable characteristic of the σ-cyclopentadienyls of platinum is that $J(Pt^{195}\text{-}H)$ is 25Hz, and this value is much greater than that of the π-bonded derivatives. The chemical shift of the ring protons is also a characteristic

TABLE 15

N.m.r. parameters of σ-cyclopentadienyl complexes.

Compound	Solvent	$\tau(C_5H_5)$	$J_{(P-H)}$ Hz	$J_{(^{195}Pt-H)}$ Hz
$(Ph_3P)(CO)Pt(C_5H_5)Cl$	$CDCl_3$	3.70	4.25	31.0
$(Et_3P)(CO)Pt(C_5H_5)Ph$	C_6D_6	3.46	4.0	39.0
$(Et_3P)_2Pt(C_5H_5)Ph$	$CDCl_3$	3.86	1.1	26.0
$(Et_3P)(Ph_3P)Pt(C_5H_5)Ph$	$CDCl_3$	4.11	1.4	26.0
$[C_6H_4(AsEt_2)_2]Pt(C_5H_5)Cl$	$CDCl_3$	3.75	-	28.0
	C_7D_8	3.54	-	30.0



(1) J(Pt-H) 31.0Hz

(2) J(P-H) 4.25Hz

Cyclopentadienyl region of $(Ph_3P)(CO)Pt(\sigma\text{-}C_5H_5)Cl$ centred at τ 3.70

FIGURE 13.

feature of the complexes, being generally observed at $<4\tau$.

Despite the fact that the compounds, with the exception of $\left[(C_6H_4)(AsEt_2)_2\right]Pt(C_5H_5)Cl$, could not be isolated in the pure state, their solutions are quite stable when stored at ca.-10°. Thus, $(Et_3P)(CO)Pt(C_5H_5)Ph$ remains unchanged in d^8-toluene after 6 weeks, as shown by the n.m.r. spectrum. The σ-cyclopentadienyls of palladium are much less stable than their platinum analogues and have only a temporary existence. Addition of Et_3P to a solution of $(\pi\text{-}C_5H_5)(Et_3P)PdBr$ in C_6D_6 caused precipitation of the salt $\left[(\pi\text{-}C_5H_5)(Et_3P)_2Pd\right]Br$. In addition to this, examination of the red supernatant liquid showed a broad peak at τ 3.63. This region is characteristic of σ-bonded cyclopentadienyl derivatives and it is thought that $(Et_3P)_2Pd(\sigma\text{-}C_5H_5)Br$ is formed. After 60 minutes, the solution had darkened and the peak at τ 3.63 had disappeared. The σ-cyclopentadienyl $(Et_3P)(Ph_3P)Pd(\sigma\text{-}C_5H_5)Br$, $\tau(C_5H_5)$ 3.72, was observed as an intermediate in the reaction between Ph_3P and $(\pi\text{-}C_5H_5)(Et_3P)PdBr$, but this also decomposed readily.

For the purpose of observing the instantaneous structure of the σ-cyclopentadienyl platinum complexes

we obtained low temperature n.m.r. spectra for $(Et_3P)(CO)Pt(C_5H_5)Ph$ in both d^8-toluene and T.H.F. at -95^o, and for $(Ph_3P)(CO)Pt(C_5H_5)Cl$ in d^8-toluene at -95^o, but did not observe any change in the structure of the cyclopentadienyl resonance. It must be assumed that the energy barrier to 'ring whizzing' is very small in these cases.

N.m.r. spectroscopy proved extremely useful in determining the stereochemistry of the platinum complexes, as has been previously described.

(b) Infrared

Introduction

Much work has been published on the infrared spectra of cyclopentadienyl derivatives of transition metals.[126] For mono-π-cyclopentadienyl complexes, the number of vibrational modes of the cyclopentadienyl ring are derived by considering the local C_{5v} symmetry of the $M-C_5H_5$ system. A simple symmetry analysis of this species shows that there should be 14 normal modes of vibration, of which 7 will be infrared active. The descriptions, intensities, and approximate frequencies of the infrared-active fundamentals localised in the C_5H_5 ring of an $M-(\pi-C_5H_5)$ group are summarised in table 16.[127] From the table it is clear that the infrared spectrum expected for the $M-(\pi-C_5H_5)$ system

TABLE 16

Infrared-active fundamental vibrational transitions for the C_5H_5 ring in a (π -C_5H_5)M system.

Type of internal coordinate change	Symmetry type	Approximate frequency, cm^{-1}	Comments
C-H stretching	a_1	3050-3100	a_1, usually very weak
	e_1		only e_1 consistently seen.
C-C stretching	a_1	ca. 1100	
	e_1	ca. 1400	
C-H out-of-plane wagging	a_1	ca. 800	usually broad absorption; position varies greatly
	e_1		
C-H in plane wagging	a_1	ca. 1000	

in the 600-3500cm^{-1} range is very simple indeed, consisting of a medium band at 3050-3100cm^{-1}, a strong band at ca. 1000cm^{-1}, and a broad, very strong band at 750-850cm^{-1}, with the possibility of two more bands at ca. 1400cm^{-1} and ca. 1100cm^{-1}.

For an M-(σ -C_5H_5) system, which can at best have C_s symmetry, there are 24 normal modes of vibration arising in the C_5H_5 group itself.[127] A very rich and complex spectrum is, therefore, expected for this class of compound, in contrast to that for M-(π -C_5H_5) derivatives.

π-Cyclopentadienyl complexes.

Table 17 lists the infrared bands, which can be assigned to the C_5H_5 ring, for the π-cyclopentadienyls prepared in this work. In the C-H stretching region only one peak is generally observed. This is due to the e_1 mode, the a_1 mode being too weak to observe.[99] In several of the spectra one or more of the other five vibrational modes could not be detected due to overlap of vibrations of other ligands with the C_5H_5 vibrations. However, the most characteristic feature, for diagnostic purposes, of the spectra of these complexes is the presence of two peaks in the region of 800cm^{-1}, associated with a C-H out-of-plane wag. The symmetry types giving rise to this vibration are an a_1 mode and an e_1 mode, and in many other

TABLE 17 Infrared absorptions of π-cyclopentadienyls

COMPLEX							
$(C_5H_5)(Et_3P)PdCl$	3100w	3065m	1390m	1105m		826s	
$(C_5H_5)(Et_3P)PdBr$	3110w	3080w	1397m	1108w		827m	767s
$(C_5H_5)(Et_3P)PdI$	3090sh	3075w	1390m	1099w		828v.s.	765v.s.
$(C_5H_5)(Pr^i_3P)PdBr$	3100m	3065sh	1385m	1105w		826s	760s
$(C_5H_5)(Ph_3P)PdBr$		3070w	1388m		1011m	826s	769s
$(C_5H_5)(Et_3P)PdPh$[a]			1412m	1108w	1009m	830m	775sh
$[(C_5H_5)(Et_3P)_2Pd]Br$		3048m	1398m	1107w		832m	786s
$[(C_5H_5)Pd(PEt_2)]_2$	3070m			1092w	995m	801m	753v.s.
$[(C_5H_5)Pd(PPr^i_2)]_2$	3090w	3030w			988w	800m	765s
$(C_5H_5)(Et_3P)PtI$	3095m	3085m	1387m	1096v.w.		826m	
$(C_5H_5)(Et_3P)PtPh$[a]		3090w		1100w		830m	
$(C_5H_5)(Bu_3P)Pt(COPh)$[a]		3090w			1009m	832m	
$[(C_5H_5)(Et_3P)_2Pt]ClO_4$		3100m	1396sh		1005m	831m	799s

(a) liquid film; (b) KBr disc; (w) weak; (m) medium; (s) strong; (sh) shoulder.

π-C_5H_5 derivatives a very broad absorption of high intensity is obtained for the two modes. The peak at higher wave number varies only from 826cm^{-1} to 834cm^{-1} in the variety of complexes listed. The more intense lower energy band is positioned at ca. 780cm^{-1} for the two nickel complexes prepared, in the 753-786cm^{-1} region for the palladium compounds, and although the band is often obscured at ca. 770cm^{-1} for the platinum derivatives it is observed at 799cm^{-1} in $[(\pi\text{-}C_5H_5)Pt(PEt_3)_2]^+ClO_4^-$

As was reported[108] for the nickel derivatives, replacement of the halogen atom of $(\pi\text{-}C_5H_5)(R_3P)MX$ (M = Pd,Pt) by a phosphine to form the salts $[(\pi\text{-}C_5H_5)M(PR_3)_2]^+X^-$ results in a shift of the lower γ(CH) band to higher wavenumber. Thus, γ(CH) values for $(\pi\text{-}C_5H_5)(Et_3P)PdBr$ and $[(\pi\text{-}C_5H_5)(Et_3P)_2Pd]^+Br^-$ are 767cm^{-1} and 786cm^{-1} respectively. For $(\pi\text{-}C_5H_5)(Et_3P)PtI$ and $[(\pi\text{-}C_5H_5)(Et_3P)_2Pt]^+ClO_4^-$, γ(CH) is ca. 765cm^{-1} and 799cm^{-1} respectively.

<u>σ-Cyclopentadienyl complexes</u>.

As predicted, the spectra of the σ-cyclopentadienyl platinum complexes contain more peaks associated with vibrations of the C_5H_5 ring than do the spectra of the π-cyclopentadienyls. Table 18 lists the data for the

TABLE 18

Data for (σ-C_5H_5)-M Complexes

$(Et_2AsC_6H_4AsEt_2)(C_5H_5)PtCl$ [b]	3055m; 1605w; 1422m; 1265m; 1078m; 960m,sh; 875s; 825w; 815m; 648s.
$(PPh_3)(CO)(C_5H_5)PtCl$ [a]	3100w,sh; 1590w; 1380m; 1264w; 1040m,sh; 1030m; 912s; 898s; 822w; 790m; 652s.
$(PEt_3)(CO)(C_5H_5)PhPt$ [a]	3080w,sh; 1608w; 1422m; 1235w; 1035m; 1001m; 960w; 878s; 820w; 735w; 638m.
$(Et_3P)_2Pt_2(C_5H_5)_2I_2$ [b]	3090m; 3065w; 3040w; 1620v.w; 1435s; 1070m; 1018s; 1008m; 848s; 830m; 800s; 640m.
$(C_5H_5)_2PdPEt_3$ [a]	3079m; 3060w; 1599m; 1435m; 1398m; 1375m; 1360w; 1332m; 1102w; 1089w; 1079m; 872m; 857m; 825s; 810m; 765s,sh; 662m; 605m.

a ----- liquid film.
b ----- KBr disc.

(σ-C_5H_5)-platinum derivatives. Many bands are again obscured by other ligand vibrations but the most characteristic feature of the spectra of the mononuclear complexes is a strong band in the 875-910cm^{-1} region. It is interesting to note that these complexes exhibit a weak peak at ca.1600cm^{-1} assignable to ν(C=C), which provides further evidence that the instantaneous structure of these derivatives has the C_5H_5 ring bound to the metal via a 2-electron covalent bond.

(c) Mass spectra

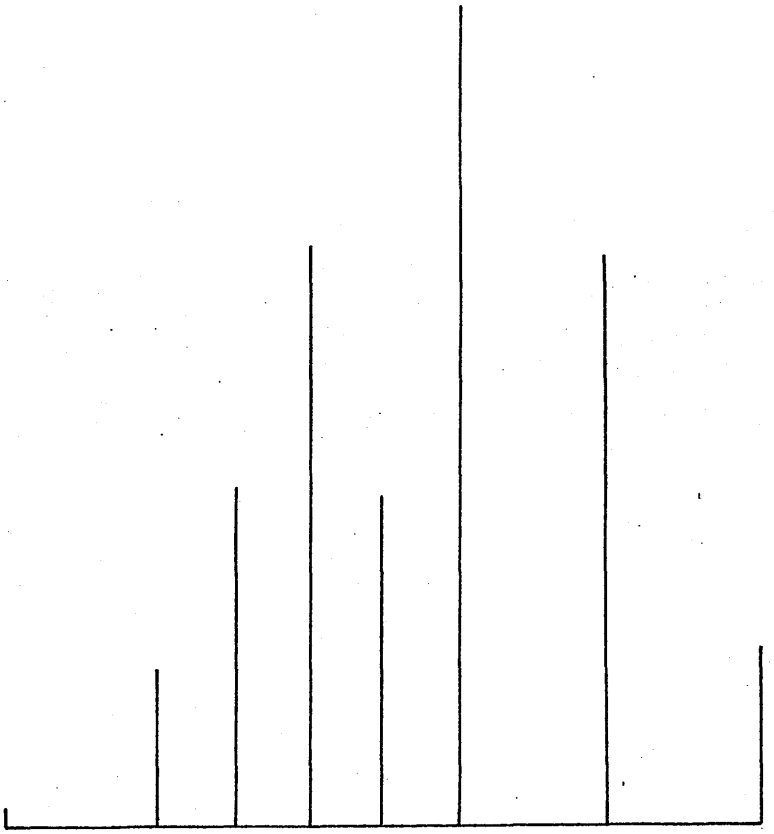
Very few results of mass spectral investigations of cyclopentadienyl palladium or platinum compounds have been reported.[128] The mass spectrum of $C_5H_5PdC_{10}H_{12}OMe$ shows that the cyclopentadienyl-palladium bond is not very strong, and the molecular ion readily loses C_5H_6 to give the ion $C_{10}H_{11}OMePd.^+$ The molecular ion of $C_5H_5PtMe_3$ fragments either by loss of the C_5H_5 ring giving $PtMe_3^+$, or by loss of methyl groups giving $C_5H_5PtMe^+$ and $C_5H_5Pt^+$.

The percentage abundancies of each stable isotope of Pd, Pt, Cl and Br are given in table 19 and figure 14 shows the calculated pattern for the Pd-Br and Pt-Cl combinations. We observed these patterns in the spectra of all complexes containing these species.

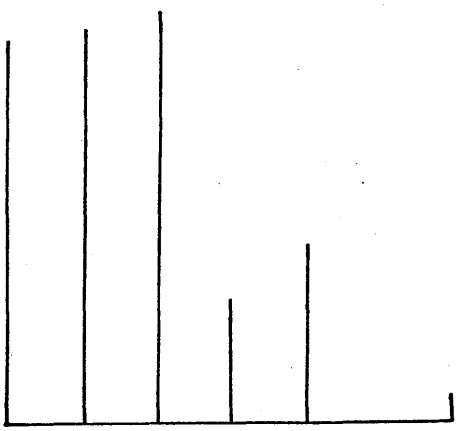
TABLE 19

ISOTOPIC ABUNDANCIES

Element	Isotope	Abundance (%)
Pd	102	0.96
	104	10.97
	105	22.23
	106	27.33
	108	26.71
	110	11.81
Pt	192	0.8
	194	32.9
	195	33.8
	196	25.3
	198	7.2
Cl	35	75.53
	37	24.47
Br	79	50.54
	81	49.46



Pd-Br combination



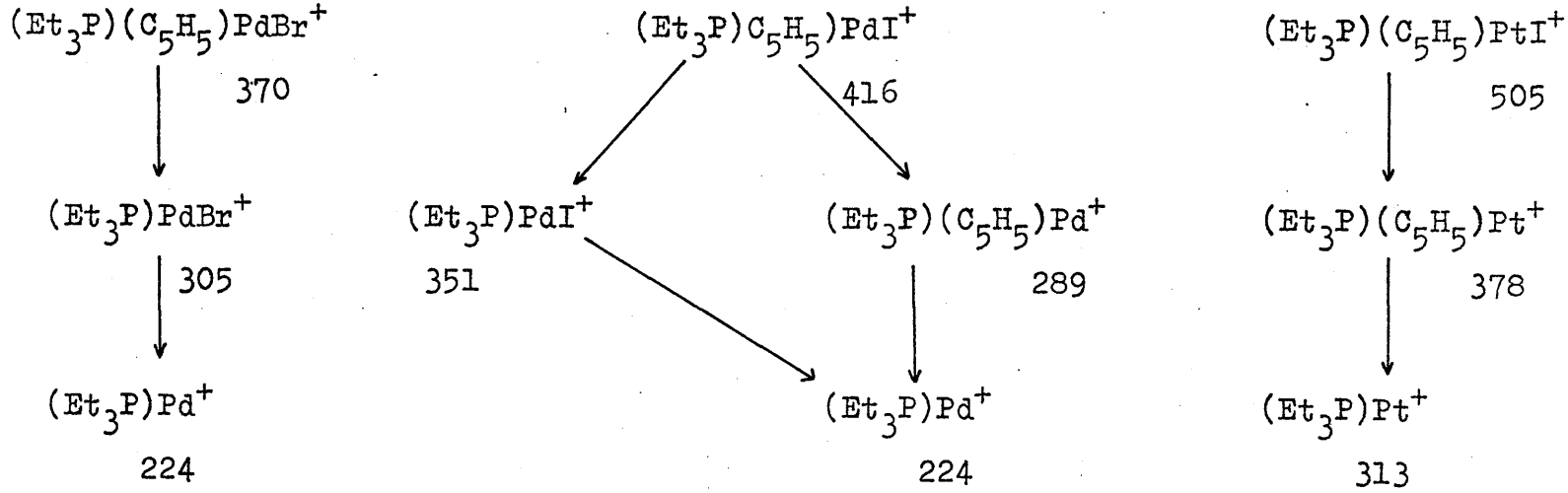
Pt-Cl combination

FIGURE 14.

The fragmentation diagrams for some of the halogen containing compounds, (π -C_5H_5)(R_3P)MX (M = Pd,Pt) are shown in figure 15. All the derivatives show molecular ions and fragments corresponding to loss of the major groups. Metal-phosphine bonds are retained most tenaciously, but there is some variation in the loss of the other groups. Initial loss of C_5H_5 is observed from (C_5H_5)(R_3P)$PdBr^+$ (R = Ph,Et), but loss of I is also apparent from (C_5H_5)(Et_3P)PdI^+, and appears to be the most important step in the fragmentation of (C_5H_5)(Et_3P)PtI^+. The loss of ethylene and ethane can be observed from the palladium species (Et_3P)PdX^+ (X = Br,I).

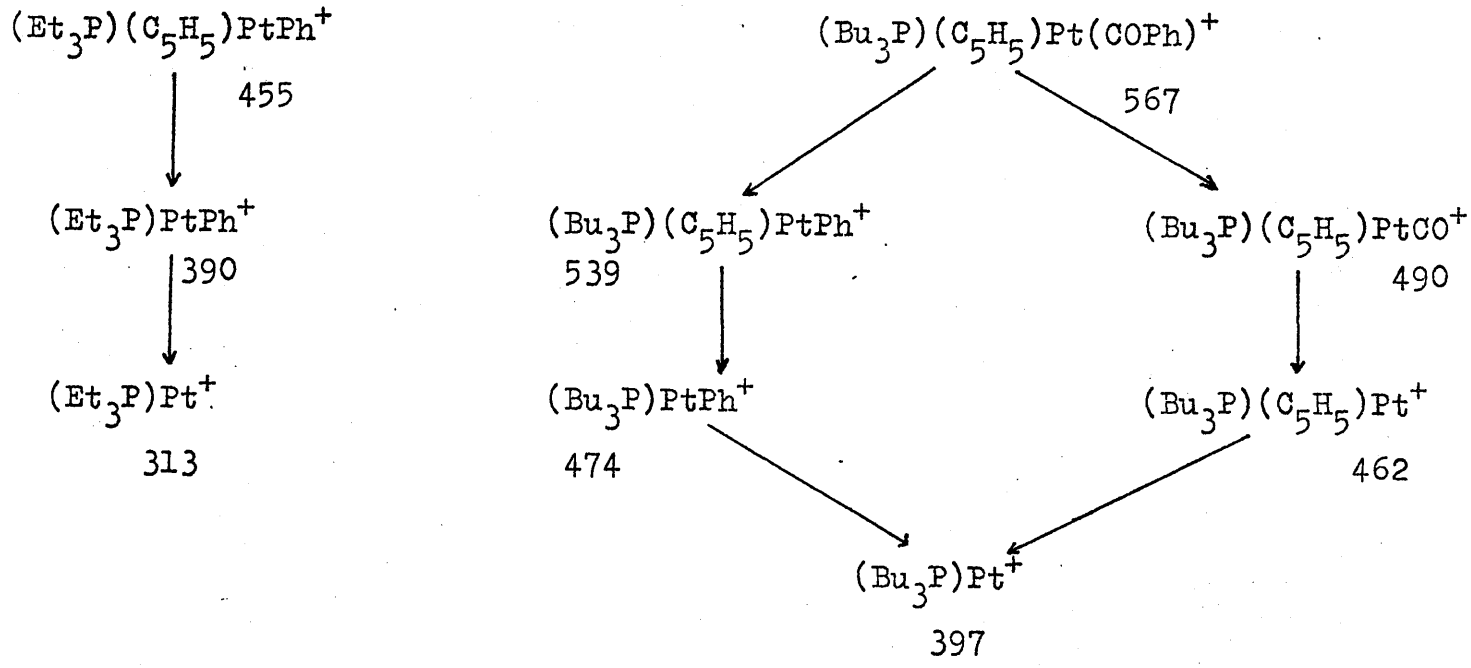
The fragmentation diagrams for two π-cyclopentadienyl platinum organo derivatives are shown in figure 16. Initial loss of C_5H_5 from (C_5H_5)(Et_3P)PtPh occurs, followed by removal of C_6H_5 to form (Et_3P)Pt^+. A metastable peak at 405, corresponding to the transition 455 $\longrightarrow$ 429, is observed and is due to elimination of C_2H_2 from the molecular ion. The ion (C_5H_5)(Bu_3P)Pt(COPh)$^+$ can fragment by loss of CO and a metastable peak at 512 corresponding to the transition 567 $\longrightarrow$ 539 is detected. The species so formed, (C_5H_5)(Bu_3P)$PtPh^+$, then follows a breakdown path equivalent to that of (C_5H_5)(Et_3P)$PtPh^+$.

FIGURE 15



Principal fragmentation paths of (π-C_5H_5)(Et_3P)MX complexes (M = Pd, Pt).

FIGURE 16

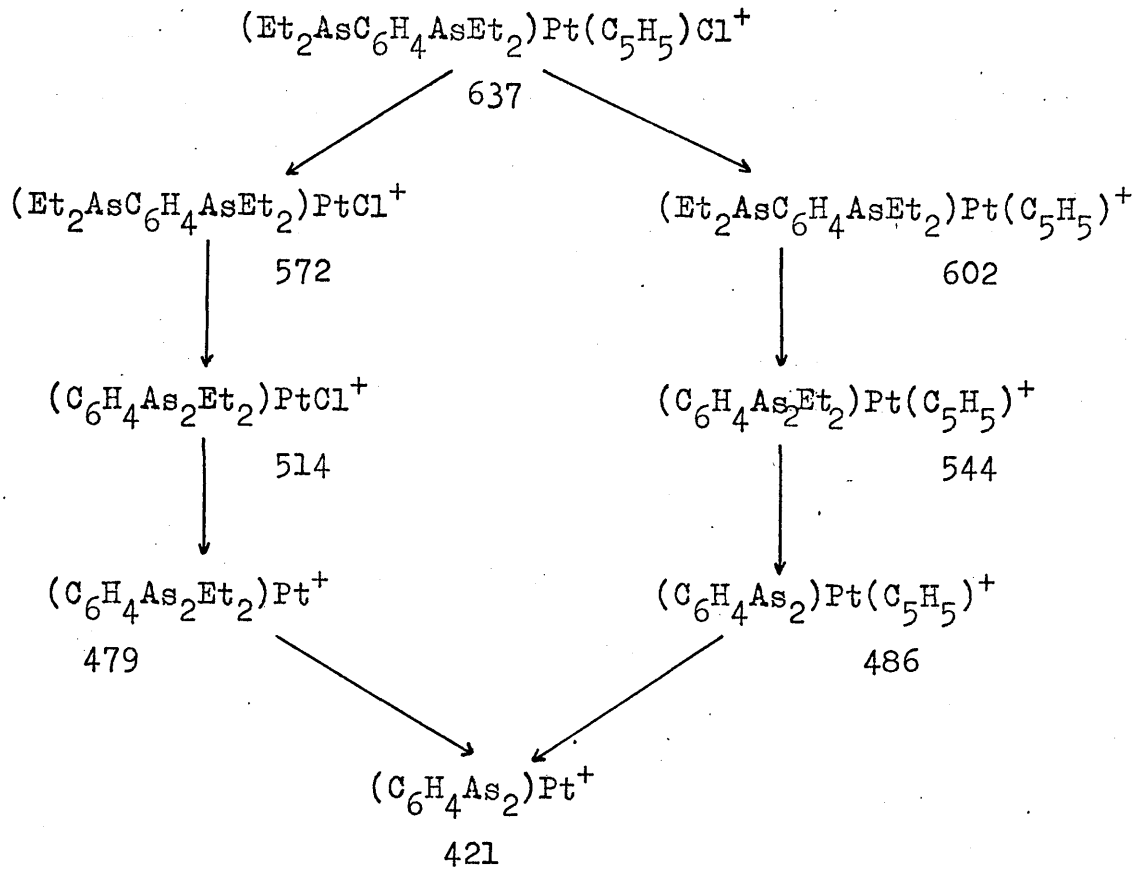


Principal fragmentation paths of $(\pi\text{-}C_5H_5)(R_3P)PtR^1$ species.

A secondary fragmentation path for $(C_5H_5)(Bu_3P)Pt(COPh)^+$ involves initial loss of Ph followed by CO elimination to give $(Bu_3P)(C_5H_5)Pt^+$. A metastable peak at 435 corresponds to the latter transition, 490 $\longrightarrow$ 462.

Breakdown paths for $\left[C_6H_4(AsEt_2)_2\right]Pt(\sigma\text{-}C_5H_5)Cl$ in the mass spectrometer are shown in figure 17. The molecular ion is again observed, and the predominant fragmentation route involves initial loss of C_5H_5. Loss of C_4H_{10} from the diarsine ligand is a common feature and platinum-arsenic bonds are retained to the last.

FIGURE 17



Principal fragmentation paths in the mass spectra of $[C_6H_4(AsEt_2)_2]Pt(\sigma\text{-}C_5H_5)Cl$.

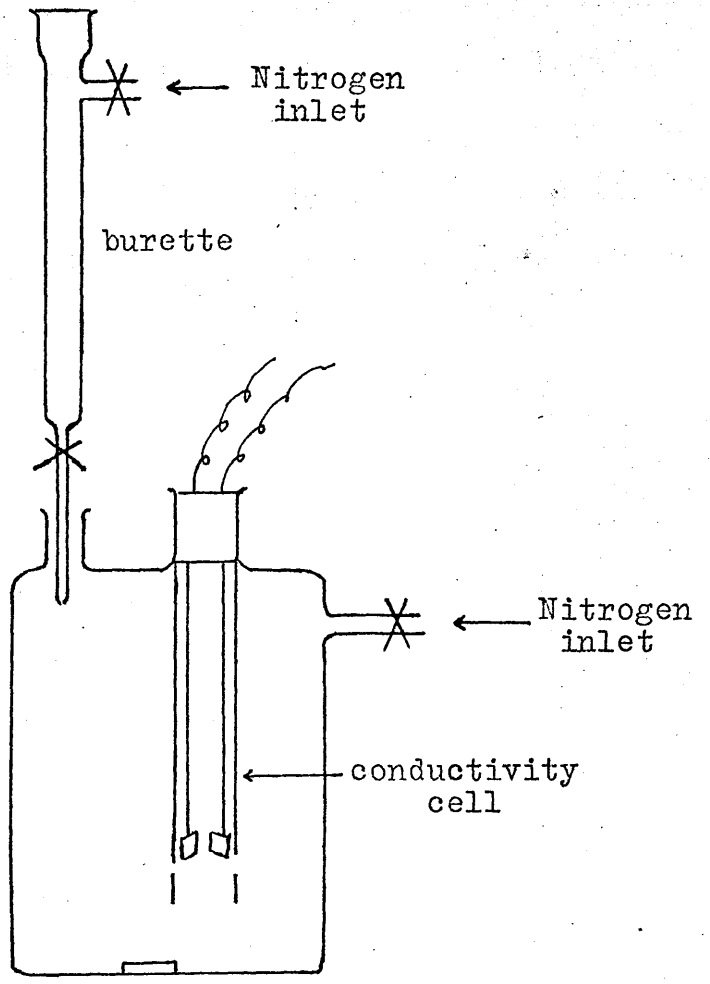
5. Experimental

All reactions were performed under an atmosphere of nitrogen. Tetrahydrofuran was dried with sodium and was freshly distilled from lithium aluminium hydride before use. Cyclopentadiene was prepared by cracking dicyclopentadiene and collecting the fraction boiling below 44°. Methanol used for conductivity measurements was dried by warming with magnesium and iodine until all the magnesium was converted to the methoxide. The pure solvent was then distilled off.

The apparatus used for the conductimetric titrations is shown in figure 18, the set-up being such that the system can always be maintained under nitrogen. Proton n.m.r. spectra were recorded at 60MHz on Varian A.60 and P.E.R.10 instruments. Low temperature n.m.r. measurements were made using a Varian H.A.100. Infra-red spectra were recorded on the P.E.457 spectrometer, and mass spectra were run on an A.E.I.MS9 or A.E.I.MS12 instrument.

Preparation of starting materials.

The starting materials $(R_3P)_2NiCl_2$ (R = Et,Ph) were prepared by standard methods[129] as was $(Ph_3P)_2HgCl_2$.[130] The halogen bridged binuclear derivatives $(R_3P)_2M_2X_4$ (R = Et, ^{i}Pr,Ph; M = Pd,Pt; X = Cl,Br,I) were synthesised



Apparatus for conductimetric titrations.

FIGURE 18.

as described in chapter 1.

Di-μ-bromobistriethylphosphinediphenyldiplatinum

$(Et_3P)_2Pt_2Cl_4$(2.8g., 3.7m.mol.) was added to PhMgBr [from Mg(0.39g., 15m.mol.) and bromobenzene (1.5ml., 15m.mol.)] in benzene (60ml.) The solution darkened immediately and was stirred for 45 minutes. After this period, the flask was cooled in an ice-bath and the excess Grignard reagent hydrolysed by water. The mixture was filtered and the layers were separated, the organic layer being dried over $MgSO_4$. Solvent was removed under vacuum and the brown residue was recrystallised three times from acetone to yield off-white crystals of di-μ-bromobistriethylphosphinediphenyldiplatinum (0.7g., 20%) m.p. 180-181°.

Di-μ-bromobistriethylphosphinediorthotolyldiplatinum

As described in chapter 1, $(Et_3P)_2Pt_2(o\text{-tolyl})_2Br_2$ was isolated from the reaction between $(Et_3P)_2Pt_2Br_4$ and $2(o\text{-tolyl})_2Hg$ in benzene.

Cyclopentadienyl thallium[99]

Thallous sulphate (5g., 10m.mol.) was suspended in an aqueous NaOH solution (15ml., 4N) under nitrogen and freshly distilled cyclopentadiene was added (3ml., 35m.mol.) The mixture was vigorously shaken for 15 minutes and the light coloured solid was filtered off. The crude cyclopentadienyl thallium was dried under vacuum and was

then sublimed at 80°/0.1m.m.Hg to yield light yellow crystals of pure cyclopentadienyl thallium (3g., 55%).

Dicyclopentadienyl mercury

Cyclopentadienyl thallium (5.4g., 20m.mol.) was suspended in T.H.F. (20ml.) The mixture was cooled to ca. -30° and a solution of mercuric chloride (2.1g., 7.5m.mol.) in T.H.F. (20ml.) was added dropwise over a period of 30 minutes. After warming to room temperature and stirring for 30 minutes, the solution was filtered. Solvent was then removed under vacuum and the light yellow residue was extracted with the minimum volume of dry ether. The ether solution was cooled to -78° to yield light yellow crystals of dicyclopentadienyl mercury (1g., 40%).

Preparation and reactions of cyclopentadienyl-nickel derivatives.

Bis-triphenylphosphinenickel II chloride and cyclopentadienyl thallium.

Cyclopentadienyl thallium (0.27g., 1m.mol.) was suspended in T.H.F. (20ml.) and $(Ph_3P)_2NiCl_2$ (0.65g., 1m.mol.) was added. The mixture was stirred at room temperature for 1 hour and the solution was filtered. Solvent was removed to leave a maroon oil which was extracted with benzene (ca. 2ml.). Light petroleum (b.p. 40-60°) (20ml.) was added and the solution was set aside at 0°. After a

few hours a number of white and maroon crystals (0.51g.) was filtered off. An n.m.r. spectrum of a portion of this material in $CDCl_3$ indicated the presence of triphenylphosphine (multiplet centred at 2.45τ) and π-cyclopentadienyltriphenylphosphinenickelIIchloride [$\tau(C_5H_5)$ 4.90(s)].

In a similar experiment cyclopentadienyl thallium (0.55g., 2m.mol.) and $(Ph_3P)_2NiCl_2$ (0.65g., 1m.mol.) in T.H.F. (20ml.) were reacted together for 3 hours at room temperature. Sublimation of the brown residue from the reaction at 80°/0.01m.m.Hg yielded dark green crystals of di-π-cyclopentadienylnickel (0.1g., 55%) m.p. 168-171°(dec)

Dicyclopentadienylmercury and bis-triethylphosphine-nickel II chloride.

Dicyclopentadienylmercury (33mg., 0.1m.mol.) was dissolved in T.H.F. (ca. 2ml.) and $(Et_3P)_2NiCl_2$ (72mg., 0.2m.mol.) was added. The mixture was stirred at room temperature for 1 hour, the solvent was removed and the residue was dissolved in $CDCl_3$(1ml.) An n.m.r. spectrum was run on the solution and this showed the presence of π-cyclopentadienyltriethylphosphine-nickel II chloride ($\tau(C_5H_5)$ 4.76 (s)).

Nickelocene, triphenylphosphine and dimethylmercury.

Nickelocene (78mg., 0.4m.mol.) was dissolved in

C_6D_6 (1ml.) and $(Ph_3P)_2HgCl_2$ (80mg., 0.1m.mol.) was added. The green solution turned to red within 15 minutes and an n.m.r. spectrum run after this time showed the presence of (π -C_5H_5)$(Ph_3P)NiCl$ [$\tau(C_5H_5)$ 5.10] and $(C_5H_5)_2Hg$ [$\tau(C_5H_5)$ 4.00].

Preparation of (π -C_5H_5)$(R_3P)ML$ (M = Pd,Pt; L = halogen, organic substituent.)

Di-μ-bromo-bistriethylphosphinedibromodipalladium and cyclopentadienyl thallium. Cyclopentadienyl thallium (2.98g., 11.14m.mol.) was suspended in T.H.F. (100ml.) and $(Et_3P)_2Pd_2Br_4$ (4.25g., 5.53m.mol.) added. The mixture immediately turned green and was stirred at room temperature for 30 minutes. The solution was filtered to remove TlBr and the solvent was then removed under reduced pressure to leave a dark green solid. This solid was recrystallised from a benzene/hexane mixture to yield dark green needles of π-cyclopentadienyltriethylphosphine-palladium II bromide (2.98g., 73%) m.p. 65-66°. (Found: C, 36.07; H, 5.44%; M(mass spectrum) 370 ($^{106}Pd^{81}Br$); $C_{11}H_{20}BrPPd$ requires C, 35.74; H, 5.46%; M, 369).

Similarly were prepared:- π-cyclopentadienyltri-ethylphosphinepalladium II chloride (from $(Et_3P)_2Pd_2Cl_4$ and C_5H_5Tl), m.p. 59-60°; found: C, 41.0, H, 6.2; $C_{11}H_{20}ClPPd$ requires C, 40.7; H, 6.2%.)

π-Cyclopentadienyltriethylphosphinepalladium II iodide (from $(Et_3P)_2Pd_2I_4$ and C_5H_5Tl), m.p. 72-73°; found: C, 31.96; H, 4.86%, M(mass spectrum) 416; $C_{11}H_{20}IPPd$ requires C, 31.74; H, 4.88%; M, 416). π-Cyclopentadienyltri-iso-propylphosphinepalladium II bromide (from $(Pr^i_3P)_2Pd_2Br_4$ and C_5H_5Tl) m.p. 111-112°; found: C, 41.03; H, 6.40%; $C_{14}H_{26}BrPPd$ requires C, 40.88; H, 6.38%). π-Cyclopentadienyltriphenylphosphinepalladium II bromide (from $(Ph_3P)_2Pd_2Br_4$ and C_5H_5Tl) m.p. 128-129° (decomp.) found: C, 53.88; H, 3.89%; M(mass spectrum) 514 ($^{106}Pd^{81}Br$): $C_{23}H_{20}BrPPd$ requires C, 53.76; H, 3.93%; M, 513).

Di-μ-iodobistriethylphosphinediiododiplatinum and cyclopentadienyl thallium.

Cyclopentadienyl thallium (0.34g., 1.27m.mol.) was suspended in T.H.F. (10ml.) and $(Et_3P)_2Pt_2I_4$ (0.72g., 0.63m.mol.) added. The mixture was stirred at room temperature for 30 minutes and filtered. Solvent was removed under vacuum to leave a brown oil, which was extracted with hexane (250ml.) leaving a yellow solid. The volume of the solution was reduced to ca. 50ml. and stored at -20°C overnight, causing precipitation of dark orange crystals of π-cyclopentadienyltriethylphosphine-platinum iodide (105mg., 17%) m.p. 68-69° (found: C,26.53;

H, 3.81%; M(mass spectrum) 505; $C_{11}H_{20}IPPt$ requires C, 26.13; H, 3.99%; M, 505).

Di-μ-iodobistriethylphosphinediiododiplatinum and dicyclopentadienyl mercury. Dicyclopentadienyl mercury (25mg., 0.075m.mol.) was dissolved in $CDCl_3$ (1ml.), under nitrogen and $(Et_3P)_2Pt_2I_4$ (44mg., 0.038m.mol.) was added. The mixture was transferred to an n.m.r. tube under nitrogen and its spectrum was recorded at intervals. Immediate examination of the ^1H n.m.r. spectrum showed the presence of C_5H_5HgI (τ 3.61) and (π-C_5H_5)$(Et_3P)PtI$ (triplet of doublets centred at τ 4.21). Some unreacted $(C_5H_5)_2Hg$ (τ 4.02) was also present. The colour of the solution gradually darkened with time and after 16 hours the intensity of the C_5H_5 resonances had decreased to half the original value.

π-Cyclopentadienyltriethylphosphinepalladium bromide and phenyl magnesium bromide. A solution of (π-C_5H_5)-$(Et_3P)PdBr$ (1.30g., 3.57m.mol.) in benzene (40ml.) was added dropwise to a cooled (5°) solution of PhMgBr [prepared from bromobenzene (1.60g., 11m.mol.) and magnesium (0.25g., 10.5m.mol.)] in ether (15ml.). The solution changed colour from green to reddish-brown and after 2 hours was almost black. At this stage, the excess Grignard was hydrolysed with degassed aqueous NH_4Cl,

the layers separated and filtered under nitrogen. The black organic portion was dried over $MgSO_4$ and filtered. The solvent was removed under reduced pressure to leave a brown oil. This oil was extracted with hexane (50ml.), the solution filtered, and solvent removed to leave π-cyclopentadienyltriethylphosphinephenylpalladium as a yellow liquid, identified by its n.m.r. and i.r. spectra. Attempted purification by vacuum sublimation led to decomposition, biphenyl being a major product.

Di-μ-bromobistriethylphosphinediphenyldiplatinum and cyclopentadienyl thallium $(Et_3P)_2Pt_2Ph_2Br_2$ (232mg., 0.25m.mol.) was dissolved in benzene (5ml.) and cyclopentadienyl thallium (150mg., 0.55m.mol.) was added. The mixture was stirred at room temperature for 60 minutes and the solution filtered. Solvent was removed to leave a yellow oil which was distilled at 60°/0.07m.m. to yield π-cyclopentadienyltriethylphosphinephenylplatinum as a yellow liquid. (Found: C, 45.47; H, 5.83%; M(mass spectrum) 455: $C_{17}H_{25}PPt$ requires C, 44.93; H, 5.54%; M = 455).

Di-μ-chloro-bistri-n-butylphosphinebisphenacyldiplatinum and cyclopentadienyl thallium. $(Bu_3P)_2Pt_2(COPh)_2Cl_2$ (174mg., 0.16m.mol.) was dissolved in benzene (5ml.) and cyclopentadienyl thallium (97mg., 0.36m.mol.) was added.

The mixture was stirred at room temperature for 45 minutes and then filtered. Solvent was removed to leave a red oil which was distilled at 70°/0.02m.m. yielding π-cyclopentadienyltributylphosphinephenacylplatinum as an orange liquid. (Found: C, 51.42; H, 6.86%; M(mass spectrum) 567: $C_{24}H_{37}OPPt$ requires C, 50.79; H, 6.61%; M = 567). The i.r. spectrum of a liquid film showed ν(CO) at 1605cm^{-1}

Di-μ-bromobistriethylphosphinedi(o-tolyl)diplatinum and cyclopentadienyl thallium. $(Et_3P)_2Pt_2(o\text{-tolyl})_2Br_2$ (50mg., 0.05m.mol.) was dissolved in benzene (2ml.) and cyclopentadienyl thallium (27mg., 0.10m.mol.) was added. The mixture was stirred at room temperature for 2 hours, then the solution was filtered and the solvent removed to leave the yellow liquid π-cyclopentadienyltriethylphosphine(o-tolyl)platinum. Its ^{1}H n.m.r. spectrum in C_6D_6 showed the following features: τ($C_5\underline{H}_5$) 4.30, $J_{(P-H)}$1.5Hz., $J_{(Pt-H)}$11.5Hz.; τ($C\underline{H}_3C_5H_4$) 7.4, $J_{(Pt-H)}$9Hz. After eight days in CCl_4 solution, the resonances due to cyclopentadienyl had disappeared.

Preparation of $[(\pi\text{-}C_5H_5)(R_3P)_2M]^+X^-$ (M = Pd,Pt)

π-Cyclopentadienyltriethylphosphinepalladium II bromide and triethylphosphine. $(\pi\text{-}C_5H_5)(Et_3P)PdBr$ (370mg., 0.1m.mol.) was dissolved in benzene (10ml.). Addition

of triethylphosphine (ca. 0.15m.mol.) to this solution caused precipitation of dark red crystals. The crystals were filtered off, washed with ether (10ml.) and dried under vacuum. Recrystallisation of the product from dichloromethane/ether gave (π-cyclopentadienylbistriethylphosphinepalladium) bromide (365mg., 75%) m.p. 87-89° (dec.). (Found: C, 41.41; H, 7.13%: $C_{17}H_{35}BrP_2Pd$ requires C, 41.78; H, 7.12%).

In a similar experiment $(\pi\text{-}C_5H_5)(Et_3P)PdBr$ (75mg., 0.02m.mol.) was dissolved in C_6D_6 (1ml.) containing 2 drops of T.M.S. Addition of 4 drops (excess) of triethyl phosphine to this solution caused precipitation of a red solid. The red supernatant liquid was transferred under nitrogen to an n.m.r. tube and ^1H n.m.r. spectra recorded at various times. The first spectrum showed a broad peak in the cyclopentadienyl region at τ 3.63 (also small doublet at τ 3.24). This region is characteristic of σ-bonded cyclopentadienyl compounds. After 60 minutes the solution had darkened and the peak at τ 3.63 had decreased almost to zero intensity.

π-Cyclopentadienyltriethylphosphinepalladium II iodide and triethylphosphine. $(\pi\text{-}C_5H_5)(Et_3P)PdI$ (12mg.) was placed in the apparatus shown in figure 18 and MeOH

(40ml., K = 0.25 x 10^{-5}ohm^{-1}cm^{-1}) added, forming a solution of concentration 0.57 x 10^{-3}M. The conductivity of this solution was determined. Triethylphosphine (9.5 μl., 7.60mg.) in MeOH (11ml.) was added in small portions by means of the burette, the solution being well stirred after each addition. Conductivity readings were taken after each addition. A graph of conductivity (ohm^{-1}cm^{-1}) versus volume added (ml.) was plotted and is shown in figure 8. The end-point corresponds to the addition of 1 equivalent of triethylphosphine and formation of (π-cyclopentadienylbistriethylphosphine-palladium) iodide. The value of the equivalent conductance of the salt was calculated as 103 ohm^{-1}cm^{-2}, corresponding to a 1:1 electrolyte with a large cation.

Triethylphosphine solutions were also added to dilute methanolic solutions of (π-C_5H_5)(Et_3P)PdCl and (π-C_5H_5)(Et_3P)PtI. Graphs of conductivity versus volume added were plotted, and the equivalent conductances of [(π-C_5H_5)(Et_3P)$_2$Pd] Cl and [(π-C_5H_5)(Et_3P)$_2$Pt] I found to be 108 ohm^{-1} cm^{-2} and 99 ohm^{-1} cm^{-2} respectively.

π-Cyclopentadienyltriethylphosphinepalladium II bromide and triphenylphosphine. Triphenylphosphine (26mg., 0.01m.mol.) was dissolved in C_6D_6 (1ml.) containing T.M.S., and (π-C_5H_5)(Et_3P)PdBr (37mg., 0.01m.mol.) added.

The solution, which changed from green to yellow-brown within 10 minutes, was transferred to an n.m.r. tube under nitrogen and spectra recorded at various times.

The first spectrum, after 15 minutes showed peaks in the cyclopentadienyl region at τ 3.72, τ 4.47 (doublet, $J_{(PH)}$ 2.5Hz.), τ 4.58 (doublet, $J_{(PH)}$ 2.5Hz.) in intensity ratio of ca. 1:4:1. The doublets at τ 4.47 and τ 4.58 corresponded to $(\pi\text{-}C_5H_5)(Et_3P)PdBr$ and $(\pi\text{-}C_5H_5)(Ph_3P)$-PdBr respectively (cf. authentic samples). The peak at τ 3.72 may be due to $(Et_3P)(Ph_3P)Pd(\sigma\text{-}C_5H_5)Br$.

After 2 hours the solution had darkened considerably and resonances of interest were at τ 3.65, τ 4.47, τ 4.80 and τ 7.0. The peaks at τ 3.72 and τ 4.58 had disappeared and the doublet at τ 4.47 was present in greatly reduced intensity. The peaks at τ 3.65 and τ 7.0 are due to C_5H_6. Decomposition was complete after 4 hours.

Bistriethylphosphinepalladium II bromide and cyclopentadienyl thallium. $(Et_3P)_2PdBr_2$ (125mg., 0.25m.mol.) was dissolved in chloroform (5ml.). Cyclopentadienyl thallium (68mg., 0.25m.mol.) was added and the mixture was stirred at room temperature for 3 hours. The red-brown solution was filtered, the solvent removed and an n.m.r. spectrum of the residue was recorded in $CDCl_3$. A triplet, in the

cyclopentadienyl region, at 4.17τ ($J_{(PH)}$2Hz.) was observed due to the presence of (π-cyclopentadienylbis-triethylphosphinepalladium) bromide (c.f. authentic sample).

Cis-bistriethylphosphineplatinum II chloride and cyclopentadienyl thallium. Cis-$(Et_3P)_2PtCl_2$ (540mg., 1.08m.mol.) was suspended in T.H.F. (15ml.), cyclopentadienyl thallium (295mg., 1.09m.mol.) added, and the mixture stirred at room temperature for 3 hours. The cherry-red solution was filtered and solvent removed under vacuum leaving a black tar. The ^1H n.m.r. spectrum of this material in $CDCl_3$ showed a triplet of triplets in the cyclopentadienyl region centred at τ4.13 ($J_{(P-H)}$2.0Hz, $J_{(Pt-H)}$11Hz), indicating formation of $\left[(\pi\text{-}C_5H_5)(Et_3P)_2\bar{P}t\right]$ Cl. Sodium perchlorate monohydrate (150mg.,1.2m.mol.) in acetone (5ml.) was added to the product and the mixture was stirred at room temperature for 4 hours. The solution was filtered and solvent removed. The black residue was then washed with water (5ml.), dried under vacuum and extracted with $CHCl_3$ (5ml.). The red solution was filtered. The solution was cooled to -78° for 6 hours causing precipitation of red-brown crystals. The crystals were collected by rapid filtration and dried under vacuum. to give (π-cyclopentadienylbistriethylphosphineplatinum) perchlorate (50mg., 8%) m.p. 180-182° (dec.). (Found:

C, 33.82; H, 5.62%: $C_{17}H_{35}ClO_4P_2Pt$ requires C, 34.24; H, 5.92%). Infra-red vibrations associated with ClO_4^- were found at 1085cm^{-1}, 922cm^{-1} and 620cm^{-1} (ref. 131).

A similar experiment performed in benzene led only to decomposition.

Preparation of σ-cyclopentadienyl derivatives.

Orthophenylenebisdiethylarsineplatinum II chloride and cyclopentadienyl thallium. Cyclopentadienyl thallium (280mg., 1.04m.mol.) was suspended in T.H.F. (15ml.), $(Et_2AsC_6H_4AsEt_2)PtCl_2$ (600mg., 0.98m.mol.) added and the mixture stirred at room temperature for 24 hours. The yellow solution was filtered and solvent removed to leave a yellow solid, which was extracted with toluene (20ml.). The solution was maintained at -20° for 3 days. The precipitate was collected by filtration and dried under vacuum to yield mustard-coloured crystals of o-phenylene-bisdiethylarsine-σ-cyclopentadienylplatinum II chloride (128mg., 20%) m.p. 139-142° (dec.). (Found: C, 35.12; H, 4.74%; M(mass spectrum) 637 (^{195}Pt ^{35}Cl): $C_{19}H_{29}As_2ClPt$ requires C, 35.56; H, 4.60%: M, 637.5).

Cis-triphenylphosphinecarbonylplatinum II chloride and cyclopentadienyl thallium. Cyclopentadienyl thallium (80mg., 0.3m.mol.) was suspended in benzene (5ml.), cis-$(PPh_3)(CO)PtCl_2$ (165mg., 0.3m.mol.) added and the mixture

stirred at room temperature for 45 minutes. The orange solution was filtered and solvent removed to yield a waxy solid (ν(CO) 2080cm^{-1}). I.r. and n.m.r. spectra are consistent with the σ-bonded complex, triphenylphosphine-carbonyl-σ-cyclopentadienylplatinum II chloride. (See tables 15 and 18). Attempts to recrystallise this compound led to loss of the cyclopentadienyl group, and formations of species with ν(CO) at 2050cm^{-1} and 1805cm^{-1}. No change was observed in the ^{1}H n.m.r. spectrum in d^8-toluene down to -95°.

In a similar experiment cyclopentadienyl thallium (54mg., 0.2m.mol.) was suspended in chloroform (3ml.) and cis-$(Ph_3P)(CO)PtCl_2$ (110mg., 0.2m.mol.) added. The mixture was stirred at room temperature for 30 minutes, then filtered and the solvent removed.

The ^{1}H n.m.r. spectrum of the orange residue showed, in addition to the main product $(Ph_3P)(CO)Pt(\sigma\text{-}C_5H_5)Cl$ (τ 3.7), a set of triplets centred at τ 4.12 ($J_{(^{195}Pt\text{-}H)}$ 13Hz) believed to be due to $[(Ph_3P)(\pi\text{-}C_5H_5)Pt(CO)]$ Cl.

π-Cyclopentadienyltriethylphosphinephenylplatinum and carbon monoxide. $(\pi\text{-}C_5H_5)(Et_3P)PhPt$ was prepared as previously described from cyclopentadienyl thallium (90mg., 0.33m.mol.) and $(Et_3P)_2Pt_2Ph_2Br_2$ (150mg., 0.16m.mol.) in benzene (5ml.). Carbon monoxide was bubbled through

the solution of (π-C_5H_5)(Et_3P)PhPt in benzene (15ml.) for 18 hours at room temperature. The yellow solution changed to green and a slight deposit of metal formed. The solution was filtered and solvent removed to leave carbonyltriethylphosphinephenyl-σ-cyclopentadienyl-platinum II as a green-brown liquid [ν(CO) 2065cm^{-1}] i.r. and n.m.r. spectra support this formulation; see tables 15 and 18. The compound decomposed during attempted purification. No change in the proton n.m.r. spectrum was observed at -80° in d^8-toluene or T.H.F.

π-Cyclopentadienyltriethylphosphinephenylplatinum and triethylphosphine. (π-C_5H_5)(Et_3P)PhPt, prepared as previously described from cyclopentadienyl thallium (162mg., 0.6m.mol.) and $(Et_3P)_2Pt_2Ph_2Br_2$ (250mg., 0.28m.mol.) was dissolved in $CDCl_3$ (1ml.) containing T.M.S. 4 drops of triethylphosphine (excess) were added causing the solution to change from yellow to crimson. The solution was transferred to an n.m.r. tube under nitrogen. Immediate examination of the ^1H n.m.r. spectrum showed a triplet of triplets centred at τ 3.86 ($J_{(PH)}$1.1Hz, $J_{(PtH)}$26Hz), consistent with the formation of trans-bistriethylphosphine-σ-cyclopentadienylphenylplatinum. The solution decomposed after several hours.

π-Cyclopentadienyl(triethylphosphine)phenylplatinum and triphenylphosphine. (π-C_5H_5)(Et_3P)PhPt, prepared as

previously described from cyclopentadienyl thallium (90mg., 0.33m.mol.) and $(Et_3P)_2Pt_2Ph_2Br_2$(150mg.,0.16m.mol.), was dissolved in $CDCl_3$ (1ml.) containing T.M.S. Triphenylphosphine (70mg., 0.27m.mol.) was added and the solution transferred to an n.m.r. tube under nitrogen. ^1H n.m.r. spectra were recorded at intervals.

After 2 hours 60% of starting material was still present (triplet of doublets centred at τ 4.30). In addition to this a triplet of triplets centred at τ 4.11 was observed ($J_{(PH)}$1.4Hz, $J_{(PtH)}$26Hz). This is consistent with formation of the species (triphenylphosphine) (triethylphosphine) (σ-cyclopentadienyl) phenylplatinum. The reaction did not go to completion unless excess Ph_3P was present, when decomposition occurred.

In a similar reaction the Ph_3P was replaced by Ph_3As. No reaction was observed after 10 days.

π-Cyclopentadienyltriethylphosphineplatinum II iodide and carbon monoxide. (π-C_5H_5)(Et_3P)PtI (80mg.) was dissolved in benzene (10ml.) and carbon monoxide bubbled through the solution for 60 minutes. The solution changed colour from dark orange to light yellow and solvent was removed under vacuum to leave a yellow liquid. I.r. and n.m.r. spectra suggested the formation of (Et_3P)(CO)Pt-(σ-C_5H_5)I (ν(CO) 2065cm^{-1}) but the complex could not be

isolated.

Reactions between (π-C_5H_5)(Et_3P)MX (M = Pd,Pt) and cyclopentadienyl thallium.

π-Cyclopentadienyltriethylphosphinepalladium II bromide and cyclopentadienyl thallium.

(π-C_5H_5)(Et_3P)PdBr (80mg., 0.22m.mol.) was dissolved in benzene (2ml.) and cyclopentadienyl thallium (60mg., 0.22m.mol.) added. The suspension was stirred at room temperature for 2.5 hours, filtered, and solvent removed under vacuum to leave a green-brown oil. Attempts to purify this product by distillation led to decomposition. On the basis of n.m.r., i.r. and mass spectra it is suggested that the product has the composition (π-cyclopentadienyl)(σ-cyclopentadienyl) triethylphosphinepalladium.

π-Cyclopentadienyltriethylphosphineplatinum II iodide and cyclopentadienyl thallium. (π-C_5H_5)(Et_3P)PtI (53mg., 0.11m.mol.) was dissolved in benzene (3ml.) and cyclopentadienyl thallium (30mg., 0.11m.mol.) added. The suspension was stirred at room temperature for 2.5 hours. The solution, which had darkened, was then filtered and solvent removed to leave a red gum. The n.m.r. spectrum of this product, in C_6D_6 showed some peaks in the 4.3-4.5τ region but their intensity was very small compared to that

of the peaks associated with the ethyl protons of the Et_3P ligand. No product could be isolated from the solution, which gradually decomposed with time.

Reactions between $(\pi\text{-}C_5H_5)(R_3P)MX$ (M = Pd,Pt) and hydrazine hydrate.

π-Cyclopentadienyltri-isopropylphosphinepalladium II bromide and hydrazine hydrate. $(\pi\text{-}C_5H_5)(Pr^i_3P)PdBr$ (0.82g., 2m.mol.) was dissolved in methanol (5ml.), and $N_2H_4H_2O$ (ca. 1.5ml.) was added. The solution immediately changed colour from green to red with evolution of gas, and was stirred at room temperature for 45 minutes. Dilute HCl was then added to acidify the solution and the product was extracted with benzene (20ml.). The layers were separated, the organic layer dried over $MgSO_4$ and solvent removed leaving a red-brown solid. This solid was dissolved in ca. 100ml. of light petroleum (b.p. 40-60°) and the solvent reduced to small volume. The solution was set aside at -20° overnight to yield dark red needles of di-μ-diisopropylphosphido-di-π-cyclopentadienylpalladium (0.2g., 30%) m.p. 133-134°(dec.) (Found: C, 50.63; H, 7.65%: $C_{28}H_{52}P_2Pd_2$ requires C, 50.75; H, 7.85%).

Di-μ-diethylphosphido-di-π-cyclopentadienyl-palladium was similarly prepared from

(π-C_5H_5)(Et_3P)PdBr and $N_2H_4H_2O$, m.p. 109-112°. (Found: C, 42.71; H, 5.96: $C_{18}H_{20}P_2Pd_2$ requires C, 41.48; H, 4.84%).

A similar reaction between (π-C_5H_5)(Et_3P)PtI and excess $N_2H_4H_2O$ produced a yellow, unstable solid which showed no resonances associated with cyclopentadienyl groups in the n.m.r. spectrum.

Preparation of $C_{20}H_{20}Pt_2$

$PtCl_2$ (2.7g., 10m.mol.) was added to C_5H_5Na prepared by the method of King[132] from Na (0.7g.,30m.mol.) and C_5H_6 (3.8ml.) in T.H.F. (30ml.) The suspension was stirred at 0° for 1 hour, filtered and solvent removed under vacuum. The black solid was extracted several times with 50ml. portions of pentane. From the first extracts, an off-white crystalline compound was isolated. This organic material is thought to consist of a mixture of cyclopentadienyl chloride derivatives. The dark green platinum complex, $C_{20}H_{20}Pt_2$, was obtained from the remaining extracts (0.15g., 5%) m.p. 131-132°.

$C_{20}H_{20}Pt_2$ and carbon monoxide

$C_{20}H_{20}Pt_2$ (50mg.) was dissolved in benzene (3ml.) and carbon monoxide bubbled through the solution for 45 minutes,

causing a colour change from green to red. The solvent was removed to leave a rust coloured solid. The mass spectrum of this material gave the molecular ion at 576 corresponding to $(C_5H_5)_2(CO)_2Pt_2^+$, and the ^1H n.m.r. of the complex in $CDCl_3$ was identical to that of an authentic sample of $[(\pi\text{-}C_5H_5)Pt(CO)]_2$[118].

$C_{20}H_{20}Pt_2$ and tertiary phosphines

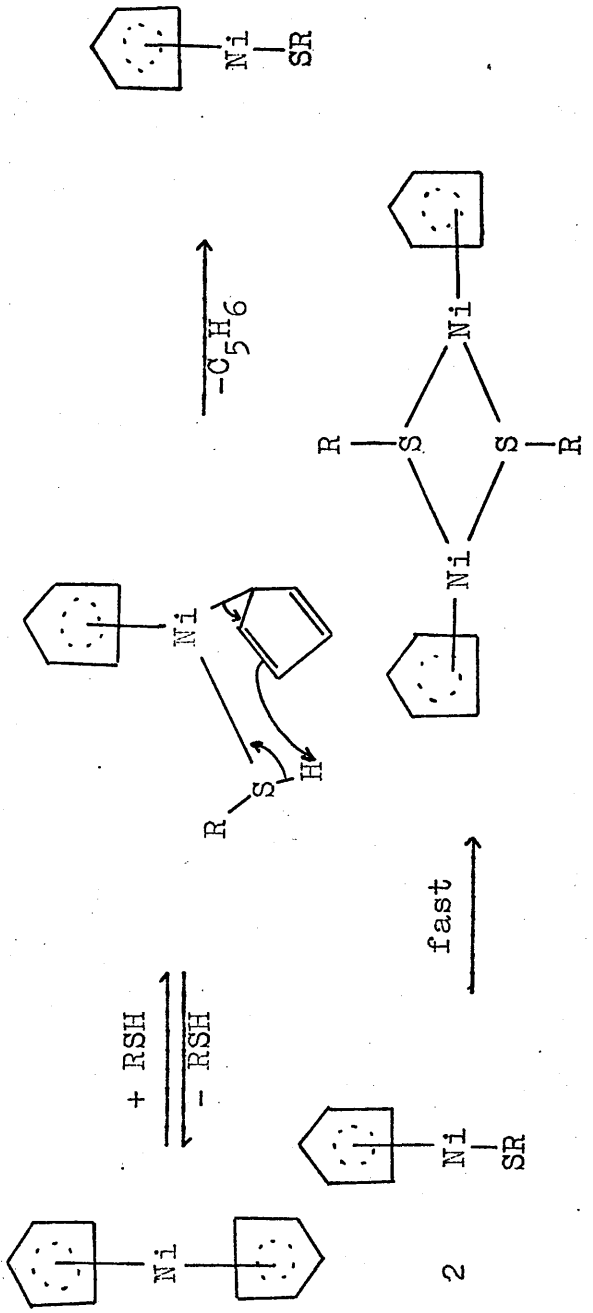
Two equivalents of tertiary phosphines Ph_3P and Bu_3^nP were added to one equivalent of $C_{20}H_{20}Pt_2$ in $CDCl_3$, and the solution transferred to n.m.r. tubes under nitrogen. Immediate examination of the spectrum in each case showed that there was no platinum-cyclopentadienyl species present. Peaks associated with the free ligand, $C_{10}H_{10}$, were detected at τ 3.65, 4.24 and 7.25.

NOTE:

In section 1 of chapter 2 we proposed that the first stage of the reaction of a nucleophile (for example, a tertiary phosphine or a mercaptan) with nickelocene involves nucleophilic attack at nickel with $\pi \longrightarrow \sigma$ rearrangement of one of the coordinated C_5H_5 ligands. In the presence of a covalent compound cleavage of the resulting Ni-(σ -C_5H_5) bond readily occurs.

Very recently a paper has been published[133] which adds support to our theory. The authors have studied the kinetics of the reactions between nickelocene and mercaptans and find that the reactions follow a rate law which is first order in each reagent. The polarity of the solvent has little effect on the rate constant, suggesting that little charge development occurs in the transition state of the reaction. A comparison of rate constants for the reactions of thiophenol and S-deuteriothiophenol with nickelocene indicates that sulphur-hydrogen bond breaking occurs in the rate-determining step.

The mechanism outlined below is used to rationalise these observations.


Ni
SR
$-C_5H_6$
R
S
S
R
Ni
Ni
R
S
H
+ RSH
- RSH
fast
Ni
SR
2
Ni

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